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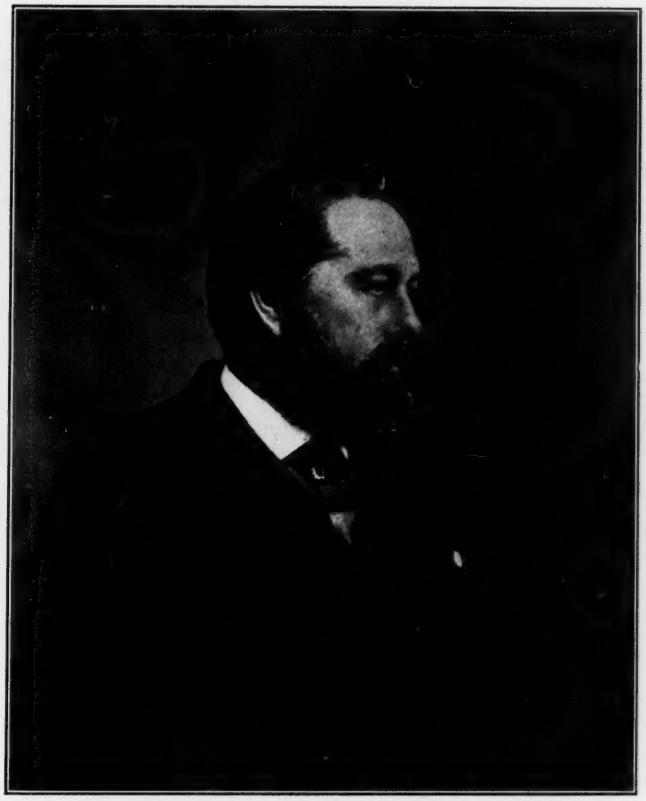

THOMAS STERRY HUNT (1826–1892)

One of the most distinguished of American chemists. He was born in Norwich, Connecticut, and studied chemistry under the elder Silliman at Yale. He served as chemist and mineralogist to the Geological Survey of Canada from 1847 to 1872, as Professor of Chemistry at Laval University, Quebec, where he lectured in French, from 1856 to 1862, and in a similar position at McGill University, Montreal, from 1862 to 1868. From 1872 to 1878 he was Professor of Geology at the Massachusetts Institute of Technology. He was President of the American Chemical Society in 1879 and 1888. He published many papers and books on various chemical subjects, chiefly on mineral chemistry and on chemical theory. He originated the theory of simple water types, and the germs of the ideas usually attributed to Gerhardt may be found in his earlier papers. His researches upon the equivalent volumes of liquids and solids were a remarkable anticipation of Dumas. He had definite and significant ideas on the real molecular complexity of mineral substances. He was one of the first, perhaps the first American chemist, to define organic chemistry as "the chemistry of carbon and its compounds." He invented, and patented in 1859, the permanent green ink which has found wide use in the printing of greenback currency.

(*Contributed by Tenney L. Davis.*)

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EDITOR'S OUTLOOK

MAY I HAVE THIS INFORMATION AT ONCE? Someone once summarized the functions of a bishop by saying that he must "suffer fools gladly and answer all letters by return mail." We have not had much experience at suffering fools gladly, but we venture the assertion that few bishops are called upon to outdo editors in answering by return mail. And sometimes it's quite a trick. The other day, in search of an answer we once knew but had since forgotten, we skimmed through a rather corpulent folder filed under the heading "Inquiries, Miscellaneous." Despite the fact that the collection constantly grows, we had almost forgotten, until thus reminded, how miscellaneous inquiries can be.

One of the prize items of our collection is a postal card bearing a date of several years ago. It says: "I have been appointed to teach chemistry in Blank High School next year. Any information you can give me on the subject would be greatly appreciated." Try answering that one by return mail; we did.

Here is another that once put us to some study. The punctuation and orthography are those of the original writer.

In the units of English on, "Vocations," which I am now studing, I am to find information, which must be relient, concerning my desired work. Finding you the editor of "Journal of Chemical Education," and a Doctor of Chemistry, I know the information which you send me will be or meet the demand. The information I would like to have, if possible, centered around Bio-Chemistry.

"What are the requirements of a good chemist to work in research laboratories?"

I would appreciate all and any information concerning the question. Because Bio-Chemistry being a new branch of Chemistry your education may be limited on the paticulars, if so, I would still value any information given.

Yours truly,

P. S. I would also appreciate it if you would sign your signature in your own handwriting at the close of the reply.

Another, less humorously couched, but difficult to answer in a word:

The Science Club, of which I am secretary, has been undecided as to how to spend their time. We have made several inspection trips and have had one guest speaker.

We would be thankful for any information which you could give us as to how we could spend our time profitably and educationally.

We are very seldom stuck for an answer of some sort, or at worst a suggestion as to a source of information, but a foreign correspondent stymied us with this one:

Oblige me with the address of some Institute or other standard authority, who can be consulted on chemical problems on the basis of a printed list of the regular charges for such information.

Here's another that wasn't quite as easy as it looks:

I am in my third year of high school and, upon entering college, desire to take a course in chemistry leading to the degree of Bachelor of Chemistry or its equivalent.

Please send me a list of the colleges offering the best chemistry courses.

We don't know who first devised a general-information test, but we think he must have got the idea from an editor. Spring these on some complaisant victim in rapid succession.

Could you kindly send me or tell how I can produce a colloidal graphite?

Will you kindly tell me what term is used to describe elements that may either lose or gain electrons and, also, what chemical meanings may the terms "amphoteric" and "metalloid" have?

Will you please outline for me a procedure that could be carried out in the laboratory for producing Bakelite?

What chemical substance secreted by fly maggots effects the healing of indolent ulcers? I am interested in the chemical formula and as to whether or not the product is on the market.

Please give me definite information as to how I may secure some Motion Pictures suitable for Chemistry Club work.

We want to place five different chemicals or substances of different colors in one test tube—then be able to shake the test tube thoroughly and have the chemicals return to their original positions in the test tube.

Sometimes they don't ask you; they tell you. We haven't thought up a good comeback for this one yet:

Professor Anonymous who is now a teacher of Chemistry in Blank High School, has simplified the presentation of the concept of Valence, the universal stumbling block to the understanding of the science of chemistry, to such an extent that the time required for most people to grasp the fundamental concept of relative combining powers of the atoms, is reduced from six months to five minutes or less.

And just as Dalton's work gave chemical science an impetus that sent it into every branch of industry and every realm of thought, as the winged messenger of speed in modern production; so Anonymous' simplification of valence broadens the sphere of influence of this great science by revealing its fascinating grandeur of creativeness to all mankind, whereas, it was before known only to a few.

With the Anonymous Atom as one means of introduction, young scientists of Blank are now announcing a new program of education based primarily and fundamentally upon the science of chemistry. They are giving a new interpretation to the cosmic ray discovered in Colorado by Professor Robert Millikan. They are now in position to give to the people the interpretation of Professor Sherman's food science which promises to extend man's life by seven years, and enrich his living standards in like proportion.

DIAGRAMS *of* CHINESE ALCHEMICAL APPARATUS

WILLIAM H. BARNES

McGill University, Montreal, Canada

INTRODUCTION

IN A previous paper,[1] reviewing an article by Y. Y. Ts'ao on the "Apparatus, Preparations, and Methods of Ancient Chinese Alchemists,"[2] I expressed the hope that it might be possible to arrange with Mr. Ts'ao for a complete and accurate translation of his important and interesting paper. The usual delay occasioned by correspondence with China having been increased by the fact that Mr. Ts'ao left the National Central University at Nanking during the summer of 1934 to teach chemistry in the Department of Pharmacy of the Chekiang Provincial Medical and Pharmaceutical College at Hangchow, it is only comparatively recently that contact has been made with him. Owing to the pressure of his regular duties it appears that Mr. Ts'ao unfortunately is unable to spare the necessary time for a proper translation of his paper. I am, however, grateful to him for permission to arrange for such a translation, or to use his article and diagrams as I may desire. I have, therefore, elected to present in the present paper such of Mr. Ts'ao's diagrams of Chinese alchemical apparatus as were not reproduced in the previous review,[1] omitting, however, two figures of a twelfth-century still and a mortar and pestle, respectively, which have already been reproduced independently from original sources by Professor Tenney L. Davis and Dr. Lu-Ch'iang Wu.[3]

In order to insure a reasonable degree of accuracy in the descriptions of the diagrams, the following procedure was adopted in the preparation of the present paper. Dr. Nancy Lee Swann, Curator of The Gest Chinese Research Library carefully checked each character of those portions of the previous translation by Mr. P. K. Wong and Mr. T. K. Hum (Ref. 1, p. 656) having a direct bearing on the diagrams. As this retranslation proceeded Dr. Swann and I discussed the interpretation of the Chinese characters in relation to the diagrams, the general purpose for which the apparatus had been or might have been intended, and, wherever possible, the use of similar apparatus in China at the present time. Doubtful or ambiguous points were then taken up by Dr. Swann with a native Chinese scholar. Uncertainties still remaining, or lack of information in the original text, finally were submitted to Mr. Ts'ao. Every precaution, therefore, has been taken to insure the accuracy of the present data and certain errors which inadvertently crept into the previous review[1] have been corrected in the appropriate places in the present paper.*

This paper is arranged as a series of notes on the respective figures, which latter are presented, with the omissions noted above, practically in the order in which they occur in the original.[2] Transliterations have been made according to the recognized Wade system, and to increase the usefulness of the paper as a contribution to Western data on Chinese alchemy the transliterations are followed in parentheses by the numbers of the characters in Giles' Chinese-English Dictionary.[4] No attempt has been made to give a translation of the titles of the Chinese books from which the diagrams were originally obtained. This could only be done safely after a more or less thorough examination of the books concerned. For the same reason such translations of the names of preparations as occur in the present paper are to be accepted only with caution.

Before proceeding to the diagrams it is of interest to note that Mr. Ts'ao uses the terms "*chin-tan* art" and "*chin-tan* experts" for the art and exponents of Chinese alchemy, respectively. Literally, *chin-tan* (2032, 10618) means "gold (or metal) [and] drugs (or chemicals)," but Mr. Ts'ao[5] considers that it is better to use the words untranslated. According to Ts'ao,[2] "this term *chin-tan* is first seen in Chin [dynasty, A.D. 265–419] Ko Hung's *Pao-p'u Tzû*," where a section on *Chin-tan* . . . . . opens with the following words:

"I have examined books for the nurture of human nature, collected and gathered from long search in [all] directions, to which have been added rolls of relevant material, essays and chapters as many as one thousand in number. None but considered 'change *tan*' and '*chin* melting' as the most important things

[1] BARNES, W. H., J. CHEM. EDUC., **11**, 655–8 (Dec., 1934).

[2] TS'AO, Y. Y., *Science* (Science Soc. of China, Shanghai), **17**, 31–54 (Jan., 1933).

[3] DAVIS, T. L. AND WU, L.-C., *Technology Rev.* (M. I. T.), **33** (May, 1931).

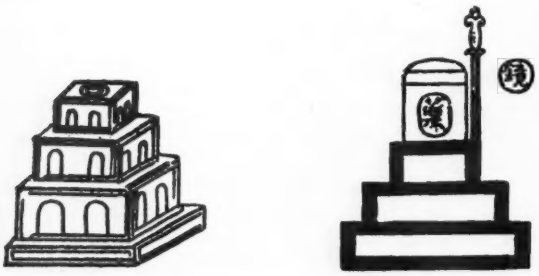
* Since the occasion does not arise elsewhere in this paper, it may be noted here that in connection with Figure 4 of the previous paper (Ref. 1, p. 658) the characters *ch'ih-chin chu-tzû* (1967, 2549) [literally, red (naked, bare, pure) metal (gold) beads] were rendered as "particles of native gold" since *chin* may mean either "gold" or "metal" and *ch'ih-chin* (red metal), although usually referring to copper, sometimes is used for gold. The *ch'ih* is red in the sense of a new-born babe and also means "naked," "bare," "pure." Hence the previous rendering of *ch'ih-chin* as "native gold." Mr. Ts'ao, however, in a private communication, translates *ch'ih-chin chu-tzû* simply as "copper beads."

[4] GILES, H. A., "A Chinese-English dictionary," 2nd ed., Bernard Quaritch, London; Kelly & Walsh, Ltd., Shanghai, Hongkong, Singapore, Yokohama, **1912.**

[5] TS'AO, Y. Y., private communication.

[in the work]. So then these two things cover the way of the *hsien* [immortals'] extreme limit [*i. e.*, final end in view]. Serve [or, eat?] these [two things] and not become an immortal, then from of old [there were] no immortals!"

Two other terms of frequent occurrence in the present paper and which it also seems best to leave untranslated are *ting* (11268) and *kuei* (6465). The former means a container or caldron sometimes with four, but more often with three, legs, or it apparently may be without legs. The latter (*kuei*) is a very general term and may simply mean box. According to Mr. Ts'ao[5] the two are used for the same purpose. The chemical for a given reaction may be placed directly in a *ting* or *kuei*, in which case the *ting* or *kuei* becomes the "reaction chamber." On the other hand the "reaction chamber" may be a small vessel which is enclosed in the *ting* or *kuei*.



A B

FIGURE 1

The two diagrams in this figure are examples of the platform, support, or altar on which the alchemical ovens were placed. In the text[2] this platform is referred to sometimes as *t'ai* (10577) and sometimes as *t'an* (10705).

Figure 1A is from the book *Tan fang hsü chih* (10618, 3440, 4716, 1783) by Wu Wu (12748, 12749). According to Mr. Ts'ao[5] this is a valuable book which describes the practical methods of Chinese alchemists. The preface is dated 1163 A.D. Regarding the *lung-hu-tan* (7479, 4920, 10618) [dragon-tiger-*tan*] platform illustrated in Figure 1A, the text of Wu Wu says that,

"On the south side of the platform and one foot away is buried one [Chinese] pound of *shêng-chu* (9865, 2550) [native cinnabar] and five inches of *hsien* (4532) [thread] over which *ts'u* (11873) [vinegar] is thrown. On the north side is buried one pound of *shih-hui* (9964, 5155) [lime; possibly, limestone], on the east side one pound of *shêng-t'ieh* (9865, 11156) [cast, or unwrought, iron], and on the west side one pound of *po-yin* (9339, 13253) [white silver]."*

The platform shown in Figure 1B is from a book *Kan ch'i shih-liu chuan chin-tan* (5844, 10064, 9959, 7276, 2711, 2032, 10618), of the Yüan (1280–1367 A.D.), or Ming (1368–1643 A.D.), period. According to Mr. Ts'ao[5] the author is unknown and the book is practical but small. The diagram shows a reaction chamber on the platform. This closed vessel was also called the *sha ho* (9620, 3954) [medicine container], *shên shih* (9819, 9974) [spirit chamber], or *hun-tun* (5239) [mixture]. The character inside the oval on the reaction chamber in the diagram is the one for "medicine." The term "mixture" presumably was applied in the sense of designating the container from that which was contained therein. The dimensions cited in the previous paper (Ref. 1, p. 657, column 1, lines 1–6) refer to the platform illustrated in this diagram. The same book† specifies that twenty-four [Chinese] ounces of cinnabar should be buried under the platform, an old sword should be impaled beside the reaction chamber, and an old mirror (in the sense of old-style, *i. e.*, probably of metal, such as bronze) should be hung on the north side of the medicine container. The sword and mirror, the latter bearing the character for "mirror," are shown in the diagram.

With regard to the linear dimensions quoted with respect to the apparatus in these and subsequent diagrams it may be noted that although the Chinese "foot" has always been divided into ten "inches" the absolute length of the former in terms of our present linear standard has varied from period to period and from one section of the country to another.[6] For example, in the fourteenth century the Chinese "foot" contained about 13 and $^1/_2$ English inches while in the sixteenth century it was equivalent to about 12 and $^1/_2$ English inches (Ref. 6, Hummel). Unfortunately, equally good references are not available for the "ounces," "pounds," "pints," and "cash" referred to in some of the quotations presented below, at least for the historical periods involved.

The section on alchemical ovens in Ts'ao's paper[2] is prefaced with the following quotation from the same book as Figure 1A. "If the *ting* has no oven it may be compared with a man who has no dwelling-place within a walled city [protected by] suburbs. How can such a man dwell in contented repose?"

This quotation emphasizes the importance attached to the oven by the alchemist as the following interpretation will indicate. In ancient China large groups of houses were surrounded by four walls usually in the form of a square or rectangle. One or more gates in each wall gave access to the city. Each of these gates was protected by a wall which joined the main city wall on each side of the gate and enclosed a portion of land in the vicinity of the gate. These outer enclosed areas were the suburbs. A single gate gave access to a suburb from the open country, so that in order to enter the city robbers were compelled to storm at least two gates. The suburbs also contained houses, but the most "contented repose" was enjoyed by one who lived within the walled city itself because of the added protection

* This quotation amplifies and makes more specific lines 14–19, column 1, p. 657, of the previous paper.[1]

† Previously confused with a book of the twelfth century (Ref. 1, p. 657, column 1, line 10).

[6] See HUMMEL, A. W., "Translation of 'Chinese foot-measures of the past nineteen centuries,' by Wang Kuo-wei," *J. Roy. Asiatic Soc., North China Branch*, **59**, 111–23 (1928); and, for periods before about the sixth century A.D., FERGUSON, J. C., "Translation of 'The fifteen different classes of measures as given in the Lü Li Chih of the Sui Dynasty history,' by Ma Hêng," Peiping, **1932**.

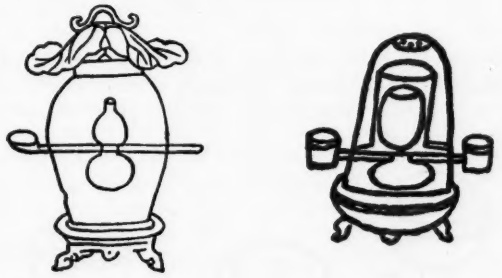
afforded by the suburbs. Such a man could attend to his daily affairs with maximum efficiency because of minimum fear of danger from without.

Figure 2 is a diagram of an oven from a book, *Chin-tan ta yao* (2032, 10618, 10470, 12889) by Ch'ên Kuan-wu (658, 6363, 12700), of A.D. 1331. According to Mr. Ts'ao[5] this is a common book in libraries in China and is of both theoretical and practical interest. The oven depicted is called a *Yen-yüeh lu* (13117, 13768, 7403) [crescent moon, or hemispherical, oven] or a *T'ai-i shên lu* (5341, 9819, 7403) [oven of the Great Primal Spirit], and is described as follows:

FIGURE 2

"The circumference of the top is about one foot two inches [*i. e.*, 12 inches]. The inside horizontal diameter at the center is one foot. It stands on a ring of 'lips' about two inches apart and two inches thick. The oven mouth opens like a crescent above the fire pan."

The "mouth" referred to in the last sentence is the opening at the bottom of the oven. The base (fire pan) probably had a depression in the center for a charcoal fire. The *ting* would be placed on the fire and the oven set down over the *ting* and fire. The lip-shaped supports and the hole in the top of the oven would permit a circulation of air over the fire. The inner wall of the oven curved from the edge of the mouth at the bottom to that of the hole in the top with the convex side toward the inside of the oven. This is the type referred to previously (Ref. 1, p. 657) as "shaped like a beehive with a flat top."



A B

FIGURE 3

The two ovens in Figure 3 are of the same type as that on the left in Figure 1 of the previous paper (Ref. 1, p. 657).* They are of *wei-chi lu* (12606, 817, 7403) [literally, not help oven] or "reverse oven" type in which the upper section holds the container and fire while the bottom of the former is kept cool by a vessel of water in the lower part of the apparatus. Appropriate tubes allow water to be introduced when desired, and also serve as outlets for steam.

The diagram in Figure 3A is from a book, *Chih ch'uan chên-jên chiao chêng shu* (1871, 2728, 589, 1302, 726, 10053), of post-T'ang authorship (probably about the tenth century A.D.[5]) although falsely credited to an earlier period. It is a theoretical book.[5]

Figure 3B shows a more elaborate *wei-chi lu* from a book, *Chin hua ch'ung pi tan ching pi chih* (2032, 5005, 2908, 9009, 10618, 2122, 8931, 1790) of A.D. 1225 by an unknown author and of theoretical interest.[5] It was employed for the preparation of the *Wu-yo t'ung hsüan-tan* (13367, 12294, 4790, 10618) [The Mysterious *Tan* of the Five Sacred Mountains].

Figure 4 shows three types of ovens from a book, *T'ai-chi chên-jên tsa tan yao-fang* (859, 589, 11454, 10618, 12958), of post-T'ang authorship (ninth to seventeenth centuries A.D.[5]). Mr. Ts'ao writes[5] that this is a valuable practical work on alchemy. The author is unknown. No details regarding these ovens are given in the original book. In Mr. Ts'ao's opinion,[5] however, *a* shows a shallow pan which is heated by hot gas (flame) above and by indirect heat below;

FIGURE 4

in *b* the dish at the top rests on the hot plate of an oven, the rectangular space below the top represents the flue, the two horizontal lines below the flue represent the grate, and the slots at the bottom indicate the ash pit; in *c* the crucible at the top is placed in such a position that only the bottom of it is heated directly by hot gases in the flue below.

Figure 5 is from the same source as Figure 1B. The two vessels *a* and *b* are reaction chambers. The characters *po-shih* (9339, 9964) on the cover of the latter signify "white stone." This material is also called *po-hu shih* (9339, 4920, 9964) [white tiger stone]

FIGURE 5

* As a matter of record it may be noted that the two diagrams in Figure 1 of the previous paper[1] are from the same source as Figure 1A of the present paper. Figure 2 of the previous paper[1] is from the same source as Figure 11, and Figures 3 and 4[1] are from the same source as Figure 3B of the present paper.

and is the type of marble or limestone which comes from Ta-li (10470, 6879), a locality in Yünnan province.[7] The cover of the reaction chamber is sealed with vinegar mixed with *ch'ih-shih-chih* (1792), which is a red clay used in making ointment. According to the original source text the water *ting*, *c*, is "made of crockery and can hold three [Chinese] pints of water. The mouth of the *ting* must be as large as the bottom of the container [*i. e.*, *a* or *b* in the diagram]. Six or seven parts of boiling water are poured in the water *ting* every time it is employed," that is, six- or seven-tenths of its volume is filled. The oven, *d*, is described as "made of mud or crockery. Its height is two feet two inches. Its breadth is one foot two inches. At the top are two holes as large as a two-cash piece. At the bottom are two holes [actually three are shown in the diagram] as large as a small copper cash."

The water container (represented in *d* as a square enclosing the character for "water") was placed below the reaction chamber (represented in *d* as an oval enclosing the character for "medicine") in the center of the oven. The water *ting* rested on a charcoal fire built on ashes. The water *ting* and reaction chamber were packed in ashes (or live coals). Hence the sevenfold repetition of the character, *hui* (5155), for "ashes," around them in the diagram *d*.

The purpose of the boiling water in the water *ting* was to keep the lower part of the reaction chamber at about 100°C.[5]

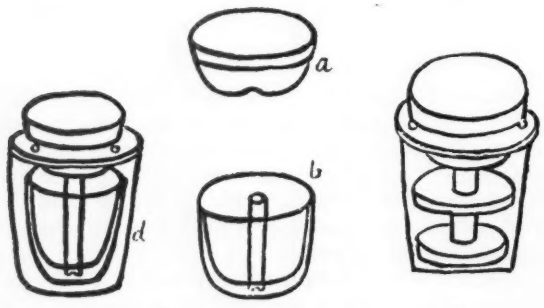


FIGURE 6

The two diagrams in Figure 6 are from the same source as Figure 3B. The assembly shown in Figure 6A was employed in the preparation of *Chin-sha huang ya ch'u tan* (2032, 9620, 5124, 12804, 2624, 10618), and that in Figure 6B was used for the preparation of *San ts'ai huan chih tan* (9552, 11496, 5080, 1892, 10618).

In Figure 6A, *a* is a silver *shui-hai* (10128, 3767) [water lake, or water tank] with a hole in the bottom. The chemicals were placed in the *yen-yüeh* (13117, 13768) [crescent moon, *i. e.*, hemispherical[5]] *ting*, *b*, which was made of red metal (*i. e.*, copper[5]) and was equipped with a jacket. The tube from the center of the bottom of the *ting* in *b* fitted the hole in the "water lake," *a*. The two parts *a* and *b* were placed together in the fire *ting*, *d*, as shown. When the apparatus was heated in an oven the jacket of *b* filled with steam and cold water could be drawn in on cooling.

The purpose of this construction is obscure and Mr. Ts'ao[5] is unable to throw any light on it.

In Figure 6B the silver "water lake" at the top had a weight of one pound and was attached to a tube of *hung-chin* (5266, 2032) [artificial gold;[5] literally, mercury metal (or gold)] which passed through the centers of two circular plates of metal (or gold), presumably to increase the cooling surface exposed [say] for the condensation of sublimates.

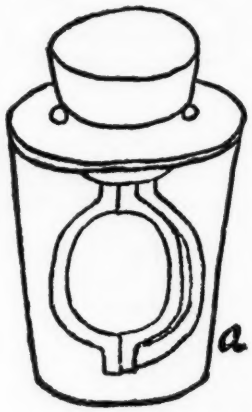


FIGURE 7

This diagram, from the same source as Figure 3B, shows a "water lake" equipped with several semicircular tubes, also presumably to insure a large cooling surface.

Mr. Ts'ao[5] volunteers the information that a book, "On Treasures," of about 900 A.D. describes twenty kinds of gold, of which only five are true gold, while the remainder, including the "artificial gold" referred to above, are false. The composition and method of preparation of this "artificial gold" are unknown.[5]

The diagram in Figure 8 is again from the same source as Figure 3B. It was used for the preparation of the *T'ung t'ien ch'ê tan* (12294, 11208, 578, 10618). It consisted of five parts *a*, *b*, *c*, *d*, *e* which were fitted together as in *f*.

Regarding this piece of apparatus a book *Chiu chuan ling sha ta tan* (2263, 2711, 7222, 9620, 10470, 10618), of the late Yüan or early Ming period (thirteenth to seventeenth centuries, A.D.) which Mr. Ts'ao[5] writes is small, practical, and of unknown authorship, says that,

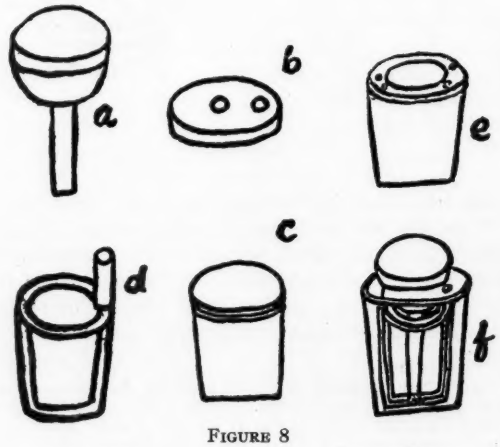


FIGURE 8

[7] "Tz'û-yüan" (*Commercial Press, Ltd., Shanghai*), section 2, p. 211.

"*Shêng-t'ieh* (9865, 11156) [cast iron] is used to make the water and fire *tings*. The [total] height is one foot two inches [*i. e.*, 12 inches]. The fire *ting* is eight inches high inside. The small mouth [at the top] is more than five inches in diameter [while] the sides plus mouth [*i. e.*, outside diameter at the top] are one foot broad. The bottom of the fire *ting* is five parts [*i. e.*, five-tenths of one inch] thick. The water *ting* is four inches high and its bottom is two parts [*i. e.*, two-tenths of one inch] thick. They [*i. e.*, the *tings*] are made by casting iron fused in a blast furnace [literally, a Ta-yeh oven]. It is important that the water and fire *tings* should fit tightly at the small mouth [of the latter]."

Ta-yeh (10470, 12990) is a locality near the great iron centers of the Hankow section of China.[8]

Figure 9 is from the same source as Figure 2, wherein it is called the *Hsüan-t'ai .ting* (4819, 10588, 11268) [hanging womb *ting*] and is described as follows:

"The *ting* has a circumference of one foot five inches with an inside diameter of five inches and a length of one foot two inches. It has the appearance of *P'eng-hu* (8901, 4954) [a fairy peak in the Eastern Sea according to ancient writings[8]] and also resembles a human body. It is divided into three sections which fit closely together. The *ting* has a hollow body. It is suspended within the oven [so that] it enters the oven evenly [to a depth of] eight inches and does not reach the bottom. It is thus in appearance like a hanging womb. It is also called the *Chu-sha ting* (2544, 9620, 11268) [vermilion ash, *i. e.*, cinnabar (?), *ting*]."

FIGURE 9

The commentator, Chang Sui (416, 10396) is cited in the original text used by Ts'ao as authority for the statement that it is also called the *Wei-kuang* (12582, 6389) [awe-inspiring, or majestic, light] *ting*.

The diagram in Figure 10A, from the book *Kêng tao chi* (6001, 10780, 906), possibly of the Ming period, shows a reaction chamber *a* inside a *kuei*.

The appearances of the *kuei* were many and varied as illustrated by *a* and *b* in Figure 10B. These two diagrams are from the same source as Figure 4. The first (*a*) is called the *Po-hu* (9339, 4920) [white tiger] *kuei* and the second (*b*) is called the *Huang-ya* (5124, 12804) [yellow sprout] *kuei*. The following recipe from the same book calls for the use of these two types of *kuei*.

[8] "Tz'û-yüan" (*Commercial Press Ltd., Shanghai*), section 2, p. 198.

"*Chin Kung Fa* (2032, 6568, 3366) [Metal (or Gold) Public Method, *i. e.*, Common Method for the Preparation of Gold].

"*Liu* (7248) [S], *Ch'ing* (2184) [a basic copper carbonate, probably azurite[6]], *Ti-nü-hsüeh* (10942, 8419, 4847) [As_2S_3], *Ti-nan-ching* (10942, 8139, 2133) [HgS], *Hung* (5266) [Hg], *P'êng* (8885) [$Na_2B_4O_7$], *T'ing* (11286) [NH_4Cl].

"Pound the aforementioned drugs about 300 times until they are as fine as powder, then stop. Afterwards pound again 100 times. Then place in the 'white tiger *kuei*' [Figure 10B, *a*]. Tend for 10 days. After this period is complete take out and pound very fine 200 times. Then place in the 'yellow sprout *kuei*' [Figure 10B, *b*]. Tend for 27 days. After [this period] is complete fuse them with a quick fire. [When the] quick [fire] ends, begin a slow [one]. That is the method."

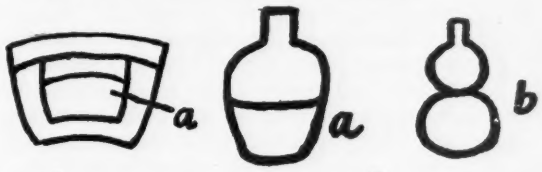


FIGURE 10

This figure illustrates three types of *kuei* (6465).

It should be mentioned that the chemicals in the foregoing list are identified by Ts'ao in his original paper (Ref. 2, p. 42), where the commentator Yüan Yü (13744, 13540) is cited as authority.

The diagram in Figure 11 is from a valuable book, *Ch'ien hung chi kêng chih pao chi-ch'êng* (1732, 5266, 1167, 6001, 1817, 8720, 906), of unknown authorship, which dates from 762 A.D., or near that time.[5] It shows a *ting* in the center of a *yung-ch'üan* (13458, 3187) [bubbling spring] *kuei*. The *ting* is completely surrounded (above, below, and on the sides) by the fire, and the oven (in this case the *kuei*) is lined with ashes as is the upper section of the oven in Figure 2 of the previous paper.[1]

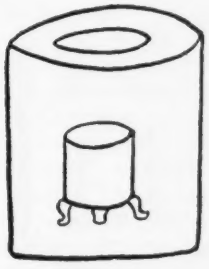


FIGURE 11

ACKNOWLEDGMENTS

I am deeply indebted to the facilities offered by The Gest Chinese Research Library and I wish to express my gratitude to the Curator, Dr. Nancy Lee Swann, for the time and trouble she has taken in connection with this paper. I am also grateful to Mr. Y. Y. Ts'ao for his kindness in allowing me to reproduce his diagrams and for his helpful collaboration in explaining and amplifying certain portions of the text of his original paper.

MIDWEST REGIONAL MEETING

THE Fourteenth Midwest Regional Meeting of the American Chemical Society will be held in Omaha next spring. Dates: Thursday, April 29–Saturday, May 1, 1937. General Chairman, Martin L. Degavre, Louisville, Kentucky; General Secretary, Nicholas Dietz, Jr., Creighton University School of Medicine, Omaha, Nebraska. This meeting should be of particular interest to chemists of the Middle West because the next two national meetings will be held in the East (Chapel Hill, North Carolina, and Rochester, New York).

HEAVY HYDROGEN *as an* INDICATOR *of the* COURSE *of* CHEMICAL REACTIONS

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University of Colorado, Boulder, Colorado

HEAVY hydrogen, or deuterium as it is frequently called, is by now too well known to require an elaborate introduction. Excellent general reviews of the history and properties of this remarkable isotope have already appeared (*1*). The ground need not be covered again. In this paper we shall treat, in somewhat greater detail than has been done heretofore, one special phase of the recent work on heavy hydrogen—a phase of particular interest to chemists—the use of deuterium as an indicator of the course of chemical reactions. It is not our purpose to treat the subject exhaustively, but rather to discuss in detail several important examples which illustrate different methods of attack. A few remarks on the general chemistry of deuterium will serve by way of introduction.

Isotopic atoms have been specified by some writers as atoms which possess different masses but identical chemical properties. This definition is somewhat unfortunate. When the isotopes of a relatively heavy element are concerned, we cannot, it is true, separate them by chemical means, but this fact does not justify a supposition that they are absolutely identical in their chemical properties. Real differences are there, but they are sufficiently minute to escape detection.

In the case of the very light elements, and in particular hydrogen, the differences of chemical properties are much more pronounced. The two isotopes of hydrogen* can, indeed, be almost completely separated by purely chemical means. Their chemical properties must, accordingly, differ to an appreciable extent. Yet deuterium should not be considered as a new element. It is truly an isotope of hydrogen, and the chemical differences are of degree rather than of kind.

In any attempt to discover the cause of the differences in the chemical properties of the two kinds of hydrogen, several factors must be considered. It is not within the scope of this paper to discuss these in detail. This has already been done adequately by Urey and Teal (*1*). It will suffice for our purposes to mention three factors, one or more of which are operative in many reactions.

1. The difference of mass of the atoms and molecules naturally gives rise to a difference of mobility of the ions in solution; and to a difference of the velocity, and hence frequency of impact, of atoms and molecules in gaseous reactions. This factor is, however, of less importance than the two to be considered subsequently.

2. There is a difference in the zero-point energies of the H— and the D— bonds in the reacting substances. Thus, D_2 has a lower zero-point energy than H_2, and hence a correspondingly greater amount of energy is necessary to rupture the D—D bond than the H—H bond.†

3. In reactions in which a potential barrier is to be passed by the quantum mechanical "tunnel" effect, there will be a different transition probability depending upon which variety of hydrogen is involved. This effect is often of great importance in reactions involving hydrogen in the atomic state.

It should be noted in passing that the above considerations would apply equally well to any isotopes, but that in the case of a heavier element the effects are much less in magnitude and hence we do not find the marked chemical differences which are unique to the isotopes of hydrogen.

The variations in the chemical properties of the hydrogen isotopes are, of course, of no small interest to the chemist. By making use of these, he can effectively separate the two isotopes. Once separated, the mass inequality becomes in a sense paramount, for the chemist finds in this very difference a means of "tagging" a specific hydrogen atom in a given compound, and of following the course of that atom throughout a series of chemical reactions; or of "tagging" certain molecules and following their history through, say, the process of human metabolism. The possibilities are great, and they have as yet been little more than tapped.

In some instances the use of heavy hydrogen as an indicator has merely served to establish a mechanism for which substantial, albeit not conclusive, evidence already existed. Such was the case in the work of Taylor and Jungers (*2*) on the photodecomposition of ammonia. The initial process in this decomposition may be represented by the equation

$$NH_3 + h\nu \longrightarrow NH_2 + H$$

The quantum yield of this reaction is, however, quite small (*ca.* 0.25 at room temperature), and this fact

* Hydrogen of mass 3, triplogen, is omitted from consideration here since it occurs in such minute quantities that its chemistry is as yet a matter of mere conjecture.

† Concerning the calculation of zero-point energies consult: GIAUQUE, W. F., *J. Am. Chem. Soc.*, **52**, 4808–15, 4816–31 (Dec., 1930).

has occasioned the assumption that the above process is reversible. This point of view received powerful support when it was found that the addition of atomic hydrogen* to the system greatly suppressed the ammonia decomposition. Nevertheless, however suggestive this evidence might be, it was not conclusive. It remained for Taylor and Jungers, making an ingenious use of the newly discovered isotope, to supply what appears to be the final bit of evidence in the proof. These investigators carried out the photodecomposition of ammonia in the presence of atomic deuterium, and followed the course of the reaction by observing the change in the absorption spectrum of the mixture. As the investigation proceeded, a progressive change occurred in the spectrum from that of pure NH_3 to that of an equilibrium mixture of NH_2D, NHD_2, and ND_3. The deuterium had undeniably replaced ordinary hydrogen in the ammonia molecules, but there still remained the possibility that this result had been effected by reactions of the type

$$NH_3 + D \longrightarrow NH_2D + H$$

This alternative was easily ruled out by conducting the experiment under conditions identical to those previously existing, except that light of the wavelength responsible for the photodecomposition of the ammonia was absent. There remained only the conclusion that the deuterium had entered the ammonia molecule by way of the reverse reaction.

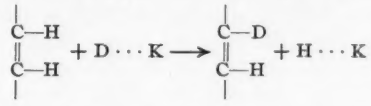
In some cases the use of deuterium or its compounds led to something definitely new, or for the most part unsuspected. Such was the result of attempts to hydrogenate ethylene and benzene by means of the isotope. It is well known that the hydrogenation of benzene, even in the presence of a considerable amount of catalyst, is a difficult and slow process. But are we justified in stating that there is little tendency for hydrogen to react with benzene under these conditions? It is quite conceivable that a rapid reaction, namely, an interchange between the hydrogen of the gas and that of the benzene, is taking place during the hydrogenation—yet the ordinary methods of chemical analysis would be quite powerless to detect it. We shall presently see that such an exchange reaction, relatively quite rapid, actually accompanies the hydrogenation. Indeed, the two reactions are merely different culminations of the same primary process.

The preliminary investigation was carried out by Horiuti, Ogden, and Polanyi (*3*) as follows. A measured amount of hydrogen of known deuterium content was employed for the hydrogenation. After the process had continued for a prescribed time, the hydrogen which remained uncombined was ignited over copper oxide and the density of the resulting water determined. From this measurement, the amount of deuterium present at the end of the experiment could be calculated with an accuracy of one part in one hundred thousand. A comparison of the amount of deuterium lost to the gas with the amount which added to the benzene led directly to the quantity of deuterium which had entered the benzene by an exchange reaction of the type:

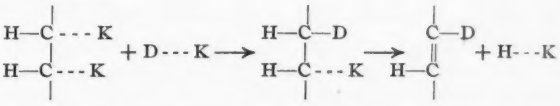
$$C_6H_6 + D_2 \longrightarrow C_6H_5D + HD$$
$$C_6H_6 + HD \longrightarrow C_6H_5D + H_2$$

Horiuti and his co-workers found that roughly, for every molecule of hydrogen which reacted by way of addition, one hundred molecules took part in exchange reactions of the type illustrated.

The investigation now resolved itself into an attempt to answer the question: "Just what is the mechanism of the exchange reaction?" Horiuti and Polanyi (*4*) were able by an investigation of the kinetics of the reaction to narrow the possibilities to two: (*a*), in which the addition and detachment occur simultaneously, and which may be formulated as follows



(where the symbol · · · K is used to represent a loose bond with the catalyst); and (*b*), in which the detachment follows the addition at some interval, according to the scheme



Reaction (*b*) assumes that the double bond has been opened by active adsorption on the catalyst.

A rigorous quantum mechanical treatment of these proposed mechanisms is, from the mathematical standpoint, impossibly complicated at present. However, Horiuti and Polanyi were able to deduce qualitatively that mechanism (*a*) would possess an appreciable activation energy, whereas in the case of (*b*) the energy of the intermediate state does not lie appreciably above that of either the initial or the final state, and hence the transition should occur with little or no true activation energy. Mechanism (*b*) is accordingly indicated. Moreover, several purely experimental facts may be advanced to substantiate this choice. We shall mention here only the one which has the most direct bearing upon the matter; namely, exchange does not occur between hydrogen and ethane under conditions which procure rapid exchange between hydrogen and ethylene† (*5*). This fact is quite understandable according to mechanism (*b*), in which the double bond plays an important rôle, but it is totally inexplicable if we accept mechanism (*a*), in which the double bond plays no part.

The complete mechanism of the reaction between benzene and hydrogen in the presence of a catalyst may now be given in four distinct steps (*4*):

* The atomic hydrogen was supplied by the familiar photochemical process:

$$Hg + h\nu = Hg^*;\ Hg^* + H_2 = Hg + 2H$$

† There seems little reason to assume that the reaction between benzene and hydrogen and that between ethylene and hydrogen occur according to different mechanisms.

1. the active adsorption of the hydrogen as atomic hydrogen;

2. the active adsorption of the benzene with the resulting opening of a double bond.

3. The transfer of a hydrogen atom to one of the carbon atoms, thus forming the half-hydrogenated state. This may be followed by:

4*a*. the elimination of a hydrogen atom from that carbon (the "exchange" reaction); or,

4*b*. the subsequent attachment of a hydrogen atom to another carbon atom (the hydrogenation reaction). Thus, the hydrogenation and the exchange reactions appear merely as different culminations of the same primary process.

The characteristic reaction between acetone and halogen has long been assumed to depend upon enolization of the ketone. The keto-enol tautomerism of several compounds has been definitely established by the isolation of the components, but in the case of acetone this has never been accomplished. The enol form, if it exists at all, must be present in very small concentrations. Nevertheless, there appeared to be good evidence that it was this form which took part in the halogenation reactions, and a mechanism of the type

$$CH_3C(OH)=CH_2 \xrightarrow{Br_2} CH_3-CBr(OH)-CH_2Br \longrightarrow CH_3\cdot CO\cdot CH_2Br + HBr, \text{ etc.}$$

was assumed.

Now, it is well established that the hydrogen of the C-O-H group is particularly susceptible to exchange reactions with D_2O, whereas hydrocarbon hydrogen takes part in such a reaction only in the presence of a catalyst, and even then only with great reluctance. These facts suggest an investigation of the reaction between heavy water and acetone. Such investigations have been carried out by Schwarz and Steiner (*6*), Klar (*7*), and others, with interesting results. The former savants, employing water of density 1.0086, found that no appreciable reaction occurs between deuterium oxide and acetone in neutral solution. In the presence of 0.6 *N* NaOH, however, the hydrogens of the acetone were largely replaced, after 18 hours, by deuterium. Schwarz and Steiner suggest the mechanism

$$H_3C-CO-CH_3 \longrightarrow CH_3-C(OH)=CH_2 \xrightarrow[D^+]{OD^-} CH_3-C(OD)=CH_2$$

$$\longrightarrow CH_3-CO-CH_2D \longrightarrow CH_3-C(OH)=CHD \xrightarrow[D^+]{OD^-} CH_3-C(OD)= \quad \text{CHD, etc.}$$

Klar carried out a similar investigation with water containing only about 0.5% deuterium oxide. His results show that in neutral solution the exchange velocity, although very small, is finite. In acid solution the velocity becomes quite appreciable and in the presence of a base it becomes relatively rapid. There is an obvious parallel between these findings and Lapworth's report that "although bromine acts very slowly in a dilute aqueous solution of acetone, yet in the presence of alkali, bromination occurs readily. It is now found that acids also accelerate the speed of substitution . . . " (*8*). Nor should we overlook the suggestion which this parallelism brings to mind; namely, that the halogenation of acetone may take place (in part, at least) by direct substitution of halogen for hydroxyl hydrogen, rather than by the postulated addition of halogen at the double bond and subsequent elimination of hydrogen halide. An investigation of the reaction between acetone and deuterium might throw light upon this point.

Very recently, Ives and Rydon (*9*) have published the results of their first attempt to unravel the very knotty problem of "three-carbon tautomerism" by means of heavy water experiments. They studied the conversion of vinylacetic acid into crotonic acid in the presence of a dilute heavy water solution of sodium hydroxide, and found that an interchange corresponding to approximately one atom of hydrogen occurred between the water and the acid. Crotonic acid itself, when treated in a similar manner, exhibited no interchange, nor did butyric acid which was employed as a control. These results, although sketchy and incomplete, are not at all in harmony with Linstead and Noble's claim (*10*) that "the tautomerism of unsaturated acids in alkaline media does not involve an additive mechanism" but comes about by a purely intramolecular rearrangement. Much more work is necessary, however, before definite conclusions can be drawn.

The use of deuterium as an indicator has even invaded the field of biochemistry. Schoenheimer and Rittenberg (*11*) have prepared several physiological compounds containing one or more deuterium atoms linked to carbon. These "heavy" compounds were found to be quite indistinguishable by the usual methods from their naturally occurring analogs. The presence of the deuterium, however, effectively tagged the molecules of these artificial compounds, and hence their fates in the body process could readily be followed.

In some preliminary experiments, mice were fed fat which had been prepared by hydrogenation of linseed oil with deuterium. In following the course of these "tagged" molecules through the process of mouse metabolism, it was found that the fat, before being utilized, is stored up in the fat deposits of the body. The fat burned is not taken directly from that absorbed, but rather from the fatty tissue.

A further observation of interest to the biochemist is that the use of deuterium has made possible for the first time the recognition of cholestenone and coprostanone as intermediates in cholesterol metabolism.

In not all cases, however, has the indicator value of deuterium been due solely or even chiefly to its mass. In some instances a comparison of the kinetics of reactions involving hydrogen and corresponding deuterium compounds has led to a greater insight into the actual

mechanisms involved. Several interesting examples of this use of deuterium as an indicator are to be found in the results of recent work on acid and basic catalysis. The general nature of these reactions seems well established by the work of Brønsted (*12*) and others. Some questions regarding the mechanism of the molecular changes involved and the function of the catalyst remained, however, unanswered until isotopic investigations were made. While it cannot be said that the use of deuterium has furnished satisfactory solutions in all cases, it has nevertheless thrown new light upon some of the old problems.

In the study of acid-basic catalysis involving deuterium, a knowledge of the comparative rates at which protons and deuterons are transferred between molecules is of considerable importance. The problem of obtaining this knowledge was solved by Wynne-Jones through an ingenious study of the neutralization in heavy water of the pseudo-acid, nitroethane (*13*). Neutralization of this compound in ordinary water solution takes place according to the scheme

$$CH_3CH_2NO_2 + OH^- \longrightarrow H_2O + CH_3CH{:}NO_2^- \quad (1)$$

In heavy water solution and in the presence of a deuteroxyl base, the reaction will be

$$CH_3CH_2NO_2 + OD^- \longrightarrow HDO + CH_3CH{:}NO_2^- \quad (2)$$

In the case of the compound CH_3CHDNO_2, neutralization in heavy water may conceivably occur either by a transfer of a proton or of a deuteron to the OD^- group. If, however, the rate of proton transfer is much greater than that of deuteron transfer, we may expect that the hydrogen will be largely replaced in preference to the deuterium. The reaction will then be

$$CH_3CHDNO_2 + OD^- \longrightarrow HDO + CH_3CD{:}NO_2^- \quad (3)$$

Finally, if the pseudo-acid $CH_3CD_2NO_2$ is employed, the reaction will be

$$CH_3CD_2NO_2 + OD^- \longrightarrow D_2O + CH_3CD{:}NO_2^- \quad (4)$$

Wynne-Jones was able to isolate almost completely each of these reactions and obtain their velocity constants under identical conditions. Table 1 gives in a condensed form the results of his investigation.

TABLE 1

NEUTRALIZATION OF NITROETHANE

Reaction	*Rate of Reaction*
(1)	39
(2)	60
(3)	36
(4)	6

Two important conclusions follow from these data: (*a*) the rate of proton transfer is at least ten times as great as that of deuteron transfer when both are determined under the same conditions (60:6), (*b*) the rate of proton transfer to a deuteroxyl ion in heavy water is about 50% greater than the rate of transfer to a hydroxyl ion in ordinary water (60:39). It may be noted in passing that the rate of transfer of the proton* in reaction (3) is only one-half that in reaction (2), which is of interest in connection with the fact that the ratio of the reaction rates is the same as the ratio of the numbers of replaceable hydrogens.

An example of the use which may be made of the above work is furnished by a consideration of the inversion of sucrose. Moelwyn-Hughes and Bonhoeffer (*14*) found that the catalytic effect of hydrogen ions in 90% D_2O solution is 60% *greater* than in ordinary water. Gross, Suess, and Steiner (*15*), in their study of the reaction in water-deuterium oxide mixtures, found a continual increase in the reaction rate with increase in D_2O content. These results, when considered in conjunction with conclusion (*a*) given above, definitely exclude as the rate-determining process the transfer of a hydrogen ion. Rather, they suggest that, if the initial process consists of the formation of a sucrose ion, $[\text{sucrose H}]^+$, then the rate of inversion is determined by the rate of decomposition of this ion.

Investigations of several other interesting reactions have proceeded along similar lines. For a consideration of these, the reader is referred to the able review by Wynne-Jones, "Use of Isotopes in Acid and Basic Catalysis" (*16*).

Heavy oxygen, O^{18}, has had a less auspicious career as a chemical detective than deuterium, but chiefly because it is so difficult to obtain the former isotope in serviceable concentrations. Nevertheless, in the hands of Polanyi and Szabo, heavy oxygen has already made one important contribution to the knowledge of mechanism. These investigators studied the hydrolysis of amyl acetate by water containing about $1/3\%$ H_2O^{18} (*17*). The amyl alcohol which resulted from the complete saponification was then analyzed, and it was found to contain only oxygen of weight 16. The heavy oxygen had entered the acid. Hence, the process of hydrolysis is definitely to be represented by the mechanism

$$AmO \mid Ac + H_2O^{18} \longrightarrow AmOH + HO^{18}Ac$$

and not by the alternative scheme:

$$Am \mid OAc + H_2O^{18} \longrightarrow AmO^{18}H + HOAc$$

This result definitely established a hydrolysis mechanism already long suspected by the organic chemist, but until now only inadequately demonstrated.

The use of isotopes as indicators of the course of chemical reaction has but barely begun. It promises to become one of the most powerful means which we possess for the study of reaction mechanism. When other isotopes come to hand in sufficient quantities, they may well prove of even more importance than deuterium. We can only guess at the progress which will be made in organic and biological chemistry when it becomes possible to "label" with ease the carbon, oxygen, and nitrogen atoms as well as the hydrogen.

* The rate of reaction (3) given in Table 1 involves both the transfer of proton and of deuteron, and hence is the sum of two reaction constants.

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The PLACE *of* COLLOID CHEMISTRY *in* CHEMICAL EDUCATION*

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DURING the departmental consideration of the revision of our fourth-year courses in chemistry, the writer undertook to ascertain how much time was being given to colloid chemistry in the universities of America. A questionnaire was mailed to those universities in Canada and the United States which give graduate work in chemistry or chemical engineering. A list of the latter was obtained from the Vocational Guidance Leaflet No. 19 of the U. S. Office of Education (1932). The questionnaire was as follows:

1. Is colloid chemistry given as a separate course(s)?.....
2. In what year? 2nd..... 3rd..... 4th..... Graduate.....
3. Compulsory..... or Elective.....?
4. Number of lectures per week.....
   Number of laboratory hours per week.....
   Length of the course in weeks.....
5. Is catalysis dealt with
   (*a*) as a separate course?.....
   (*b*) as a part of colloid chemistry?.....
   (*c*) as a part of physical chemistry?.....
   (*d*) as a part of industrial chemistry?.....
   (*e*) as a part of organic chemistry?.....

One hundred replies were received from one hundred eighteen inquiries. Seventy-three universities were found to give some eighty-two courses in colloid chemistry. Two of these are reading courses, and one, a combined lecture and seminar or discussion course. The data for the above institutions are summarized in Table 1. The omission of any university means either that no separate course in colloid chemistry is given or that the questionnaire was unanswered.

It will be seen from Column 2 that approximately three-quarters of the courses are open to undergraduates. This is to be expected. The student in chemistry or chemical engineering is continually meeting "colloidal complications" in the so-called pure chemistry courses. In analytical chemistry, for example, he gets colloidal suspensions, gelatinous precipitates, encounters errors due to adsorption or peptization of precipitates, and is perhaps introduced to adsorption indicators. In organic preparations catalysts are often used; a desired crystalline product may turn out to be a gummy or gelatinous mass. He finds that electrochemistry has to take cognizance of protective colloids and other colloidal phenomena, that industrial chemistry abounds in colloidal applications and problems, while in biochemistry a considerable portion of the text or time is given to the study of the colloidal state. A separate course for the undergraduate serves to coordinate these ramifications of colloidal chemistry in pure and applied chemistry.

It is interesting to note the distribution of these undergraduate courses in colloid chemistry according to years. In one university the course is open to second-year students, ten courses are available to juniors, while fifty are given to seniors. In fourteen universities the course is compulsory and in still others, while nominally elective, it is "practically compulsory owing to restricted choice, etc."

Twenty-seven of the eighty courses are for graduates only. Many courses are open to both seniors and graduates.

The number of courses which consist of both lectures and laboratory is forty-four. In seven more the laboratory work is elective. The average number of lectures in those courses giving no laboratory work is considerably above the mean. For all courses the average gives a total of forty-one lecture hours and forty laboratory hours.

Catalysis is dealt with as a part of colloid chemistry in thirty of the eighty courses considered. In twenty-one universities a separate course is offered. Nine of the latter are undergraduate courses. The topic is usually dealt with as a part of physical chemistry, but in thirty cases it is discussed as a part of organic, and in twenty-seven as a part of industrial chemistry.

Several of those who reported that no separate course was given in colloid chemistry at present stated that plans were under way for the introduction of such a course. In two other instances it was intimated that

* Presented to the Section on Chemical Education, Canadian Chemical Convention, Niagara, June, 1936.

the time given to colloid chemistry was to be increased. The tendency seems therefore to be toward a separation of colloid chemistry from the course in physical chemistry and its establishment as a distinct course.

TABLE 1

University	*Year given*	*Hrs./wk.* LEC.	LAB.	*Total Hours* LEC.	LAB.	*Catalysis (Quest. 5)*	*Remarks*
Alberta, Univ. of	4, 5 AE	2	6	22	66	c	Alternate years
Akron, Univ. of	AE	2	0	36	0	ce	
Baylor University	4AE	3	4	36	48	bc	
British Columbia Univ.	4AC	2	0	24	0	bdce	
Brooklyn Polytech. I.	A*	.	0	24	0	Ac	* Alternate years
Bryn Mawr College	AE*	2	13†	60	390	bc	* Given occasionally
California Inst. Tech.	4C*	2	1	18	9	Ab	* Req'd. of chem. eng's. & chemists
California, Univ. of	3, 4AE	3	....	39	....	abcde	
Case School App. Sci.	3C, AE	3	E	54	E	Ace	
Clark University	AC	2	1	36	18	c	
Colorado School Mines	AE	2	0	32	0	c	
Colorado, Univ. of	4AE	1	6	12	72	bcde	
Columbia University	3, 4E	2	0	30	0	c	
	AE	2	4	30	60	Ac	
Cornell University	4AE*	2	....	64	....	c	* From univ. calendar
Florida, Univ. of	AE	2	3	36	54	Abcde	(A) 3 lect., 18 wks.
Fordham University	AC	2	4	30	60	Ac	2 lect., 4 lab., 15 wks.
Harvard University	4AE	3	0	54	0	cde	
Holy Cross College	3C, AE	2	4	32	64	c	
Howard University	4AE	2	E	36	E		
Idaho, Univ. of	AE*	2	0	32	0	cde	* To be instituted
Illinois, Univ. of	3, 4AE	2	1*	32	16	cde	* Demonstrations
Iowa State College	4AE	2	2*	24	24	a	* Average time
Iowa State University	4AE	3	3*	54	54*	Ac	* Average time
Indiana University	4AE	2	E	68	E	Ac	(A) 2 lect., 17 wks.
Kansas State College	3, 4AE	2*	0	36	0	abcde	* To be increased
Kansas, Univ. of	AE	2	3	36	54	c	
Lehigh University	AE	3	E	45	E	Ac	(A) 3 lect., 15 wks.
Louisiana State Univ.	AE	2	0	72	0	Ace	(A), 1 semester
Manitoba, Univ. of	4C	1	3	30	75*		* Some lect. in lab. time
Maryland, Univ. of	A	2	6	64	192	Abcde	(A) 2 lect., 16 wks.
Mass. Inst. Tech.	4C*	3	0	30	0	c	* Chem. eng's.
	AE	3	6	48	96	A	(2 lect., 2 lab., 16 wks.)
Mass. State College	4AE	0	10	0	160*	c	* Reading course
	AE	1	0	10	0		Alternate years
McGill University	4AE	2	1*	52	26*	bdce	* Lab. time varies
Michigan, Univ. of	4AE	2	6	32	96	b	
	AE*	2	6	32	96		* Applied colloid chem.
Minnesota, Univ. of	4AE	2	6	64	192	cd	
Missouri School of Mines	AE	3	0	54	0	bcde	
Missouri, Univ. of	4AC	3	2	54	36	bcd	
Nebraska, Univ. of	3, 4E	2	4*	36	82*	c	* Average
New York University	4AE	2	E	30	E	c	Two courses given
N. Carolina State Coll.	4AE	3	0	36	0	c	
N. Carolina, Univ. of	2, 3, 4AC	3	2	48	32	bd	
Northwestern Univ.	AE	2	0	32	0	c	
Notre Dame, Univ. of	AE	3	0	54	0	ac	
Oberlin College	AC	2	9	36	162	bce	Chiefly c
Ohio State Univ.	4AE	3	6E	36	72E	abc	
Oklahoma Agr. & Mech. Coll.	4AE	3	0	54	0	acde	
Oregon State College	4AE	3	1	72	24	bc	
Oregon, Univ. of	4E	2	0	40	0	bcde	
Penn. State College	4E	1	5	18	90	cde	
	AE	3	0	108	0	A	
Pennsylvania, Univ. of	4C	2	0	32	0	c	
Pittsburgh, Univ. of	4AE	2	0	64	0	bcde	Alternate years
Princeton University	4E	2	3	32	48	c	
	AE	3	3	48	48		
Purdue University	4AE	3	0	45	0	bcde	
Queen's University	4C	1	3	16	25*	Ace	* Avge. (A) 2 lect., 14 wks.
	3C	0	3	0	75*	Reading course for Arts students	
Rensselaer Polytech. I.	4C	3	6	21	42	bcde	
	AC	.	....	20	20		
Rice Institute	4C*	2	4	72	144	Ac	* Chem. Eng.
Rutgers University	AE	2	2.5	72	90	c	
Saskatchewan, Univ. of	4AE	2	0	54	0	bcde	
South Dakota, Univ. of	AE	2	1	32	16	ce	
Stanford Univ.	4AE*	3	0	52	0	abcde	Three courses given successively
Syracuse University	4AE	1	3	36	108	cd	
Toronto, Univ. of	4AE	1	0	30	0		Given by Physics Dept.
Utah, Univ. of	AC	2	0	24	0	c	
Vanderbilt University	4AE	3	....	27	0	abc	
Virginia Tech. Inst.	AE	2	3	64	96	bcd	
Virginia, Univ. of	AE	2	3	64	96	c	
Washington State College	4AE	2	3	36	54	c	
Washington, Univ. of	AE	3	E	36	E	bc	
Western Ontario, Univ. of	4C	2	4	28	56	bcde	
Western Reserve Univ.	3, 4AE	1	6	18	108	bce	
West Virginia, Univ. of	4AE	2	6	36	108	bcde	
Wisconsin, Univ. of	4AE	2	0	72	0	b	
Yale University	AE	1	0	30	0	bcde	

E = elective; C = compulsory; A = graduate; a = undergraduate or unstated

† Combined lecture and seminar course.

LESSONS *from* TWELVE YEARS *of* CHEMISTRY CONTESTS*

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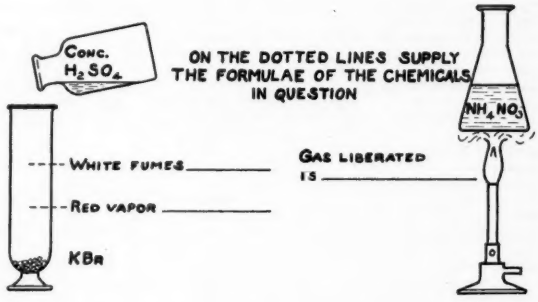
PUPILS at the secondary-school level always exhibit a keen interest when participating in an activity of a competitive nature. An opportunity for such participation was afforded the high-school students of Rhode Island by the series of annual chemistry contests which have been held at Rhode Island State College since 1924. These yearly contests have stimulated much discussion and have served to focus attention on a number of facts which should be of vital interest to any secondary-school teacher of chemistry.

The contests have occurred each year early in May as a part of the activities of the Annual Interscholastic Track Meet† which has been held for the past quarter of a century at the college. On this day about 1500 high-school pupils and their friends come to Kingston. The chemistry contest has been a valuable adjunct to the athletic competition and has added much interest to the events of the day.

For use in competition of this sort, a definite type of examination had to be developed. Furthermore, it was essential that the tests be corrected in the minimum of time. This was demanded by the fact that the awards in the chemistry contest were made at the same time that the athletic awards were given out. The general make-up of the test, therefore, was as objective as possible, and consequently permitted a wide choice in the type and form of question used.

As is well known, a large number of different kinds of objective questions have been developed for testing programs in school subjects. Only a few of the types of questions which gave rather satisfactory results will be cited herein. The true-false (plus-and-minus) question is one of the old standby types. It served well in a number of tests, although the element of guessing always entered in and had to be taken into account. A second kind of question which was employed for several years with good results was the so-called "diagram" question, as illustrated in Figure 1.



The "multiple-choice" questions, variations of which type were termed "matching" or "selective response," were found to be quite satisfactory. A serious difficulty with this sort of question lies in the elimination of the possibility of more than one correct answer when the test is made out. The best form appearing in any of the contests was that used in 1935, in which a statement could be answered by only one of three possible answers, all of which were printed, but only *one* of which was correct. The correct response was to be indicated by a plus sign in front of the statement.

Another type of question which was tried out for the first time in the 1935 contest and which gave splendid results was the so-called "analogy type." This involved a sort of proportionality between short statements or between chemical words or symbols. Three terms of such a proportionality were given and the student was required to supply the missing term. This type of question is indicated below.

Analogies

Directions: Each horizontal line represents a condensed statement, written in the style of a proportion, involving four different factors. The first three of these are given, but the fourth is to be supplied by the student and may be derived by interpreting the statement as a relationship.

EXAMPLE 1. Nitrate : NO_3 group :: Sulfite: ——

ANS. *SO_3 group*

For instance, in the first example above, read somewhat as follows: "If the nitrate is the NO_3 group, then the sulfite will be the SO_3 group," which is the correct answer and is written on the blank line provided.

EXAMPLE 2. Solid : Ice :: Liquid : —— ANS. *Water*

Another way to arrive at the answer is to read the statement in the form of a question, as, for example 2 above: "What is the liquid that corresponds to the solid, ice?" Obviously the answer is "water" and this is written on the blank line provided.

The advantage of this kind of question lies in the elimination of any but the one correct answer, provided the given three terms of the proportionality are prop-

* Presented before the Division of Chemical Education at the ninetieth meeting of the American Chemical Society, San Francisco, August 19, 1935.

† *Editor's Note.*—Recalling the use of various scholastic contests in connection with interscholastic meets in western colleges, J. W. Ince suggested to F. W. Keaney in 1923 the possibility of incorporating a chemistry contest in the events of the annual high-school meet at Rhode Island State College. Mr. Keaney became enthusiastic over the idea and, from his experience in teaching general chemistry in both high school and college, furnished the questions from 1924–1931. Dr. R. K. Carleton supplied the questions for the remainder of the period. J. W. Ince and other members of the staff, Drs. C. L. Brown, W. G. Parks, and A. A. Vernon collaborated as critics and editors.

erly selected. Experience indicates that ambiguity is more readily eliminated from this sort of question than from any other.

What about problems and equations? Certainly no test would be considered complete without them. Regarding the former, it was felt that any student graduating from a standard secondary school ought to be able to handle the so-called fundamental type problems of chemistry. Under that heading might be included the following kinds:

1. Calculation of molecular weights
2. Determination of formula
3. Percentage composition
4. Weight-calculation problems
5. Gas problems
6. Weight-volume problems
7. Molar and normal solutions
8. Molecular weights of gases

Concerning the use of equations in tests of this sort, it must be recognized that the balancing of equations demands time. In view of the fact that the total time allotted for the completion of the contest was but one and one-half hours, it can be readily seen that relatively few equations could be included in the test. Thus, again referring to the test used in 1935, twenty-five equations were given, correctly balanced, and all the student was required to do was to place a letter in a blank following the equation indicating the color or type of the gas or precipitate which was formed. In case neither was produced, the space was left blank. Some examples which follow will make this clear.

Equations

Directions: The following equations are *correctly* balanced. Place one of the following letters in the blank after each equation, indicating the character of the gas or precipitate which is formed. Read the examples before attempting to answer the questions. Write legibly.

(*a*) colorless gas (*c*) brown gas (*e*) yellow precipitate
(*b*) white precipitate (*d*) gas, fumes in air (*f*) greenish gas

EXAMPLE 1. $Ba(OH)_2 + CO_2 = BaCO_3 + H_2O$ *b*
EXAMPLE 2. $SiO_2 + 3C = SiC + 2CO$ *a*

A modification of the standard form of equation was also tried out in the 1935 contest. The formulas of two different chemical compounds or elements were given. The one at the left side of the page was the compound with which to start, and the one at the right side of the page was the substance which was finally obtained. The student was then expected to use his knowledge of different chemical reactions, and think through the necessary reactions whereby the second compound was derived from the first one which was given. A blank space was provided between the two formulas involved, and in this space the student was to put the formula for the correct compound (one only), derived from the given material, which would yield the second or required substance. Some examples of this type follow.

Completion

Directions: In each of the following questions there is a relationship indicated between three compounds (or elements). The formulas (or symbols) of two of the substances in each group are given, but the third must be supplied by the student. The substance in the left-hand column yields the material in the right-hand column in each case, but involves the necessary preparation of an *intermediate* substance, the correct formula of which constitutes the answer.

Read the examples carefully before attempting to answer the questions.

EXAMPLE 1. $BiCl_3 \ldots Bi_2S_3 \ldots H_2S$; *i. e.*, the substance derived from $BiCl_3$ that will yield H_2S is Bi_2S_3.

EXAMPLE 2. $Al \ldots Al_4C_3 \ldots CH_4$; *i. e.*, the substance derived from aluminum that will yield CH_4 is Al_4C_3.

There are several advantages to be claimed for this sort of question. In the first place there can be but *one* correct reply, provided the statements are accurate and correctly made out. Moreover they are short and direct, and necessitate clear thinking on the part of the student. On the other hand, unless a student has sufficient knowledge of the fundamental reactions of chemistry to enable him to get started, he can make absolutely no progress on this sort of question.

Since the beginning of the contest there have been numerous prizes awarded for the high-standing contestants, as well as souvenirs for all who participated in the contest. The prizes were contributed by friends of the chemistry department of Rhode Island State College and added materially to the success of the whole affair. These prizes and souvenirs included a variety of different materials, such as books on chemical topics, appropriate loose-leaf notebooks with leather covers, slide rules, chem-rules, etc.

The principal prize was the silver trophy which was awarded with the understanding that it would become the permanent possession of the high school whose teams were successful in winning the contest three years in succession. This might seem at first thought like a rather easy thing to accomplish, but it is interesting to note that during the twelve years of the contest only two trophies have been won permanently. Occasionally, during the period, prizes have been given to the teachers of the teams which ranked highest.

As to the scope of the examination, it would appear to be what nearly anyone would expect since the contestants were to come from secondary schools. Quoted from a copy of the rules and regulations is this statement:

"The ground to be covered by the examination is practically that stated in the maximum college entrance requirements for secondary schools, except that no questions upon metallurgy will be given."

It was deemed advisable to build the examination upon a good broad knowledge of chemistry, such as is demanded by college entrance, rather than to require a comprehensive knowledge of certain specific topics such as metallurgy.

Eligibility regulations were definitely stated and rigidly enforced. In the first place the contestants must be *bona fide* undergraduates of a high school or a

preparatory school, who were taken from regular classes in chemistry and who had not had more than *nine* months' training. Certification to this fact had to be made by the respective teachers. Any student who had competed once was ruled out of participation in subsequent contests as, also, were postgraduate students. It should be noted in passing that in regard to eligibility no difficulties were experienced and the teachers were always more than willing to coöperate.

A quotation from the regulations which cover the arrangement of teams and the method of computing the relative standing may be of interest.

"Each school may send a team of from three to five pupils. The sum of the three highest scores of each team will constitute the total score for that school as in the rifle shoot method, the maximum score possible being 300. Individuals from any school, however, which may not have sent a team may compete for individual honors. Alternates may take the examination but are not eligible for prizes.

Any school so desiring may enter a team of girls in addition to a team of boys, provided:

1. Not more than one team from any one school competes for the major trophy;
2. The school entering two teams states previous to the day of the contest which team is to compete for the trophy."

As previously mentioned, there have been but two team trophies permanently awarded during the entire twelve-year period. The first, a silver wash bottle, which was purchased by contributions from alumni of the chemistry courses, was won permanently in 1927 by the Pawtucket High School. Following this award, a second trophy was made available for competition by an alumnus of the college and was known as the Williams trophy. This was a silver loving cup of beautiful design, which remained in competition during the succeeding eight years. The cup was finally won permanently by the Westerly High School in 1935, and thereby ended competition for the second time, at least temporarily.

The original purpose of the contests was to create an interest among the high-school pupils of the state in the science of chemistry. Many facts indicate that this objective has been achieved. Furthermore, it would seem to the writers that a healthy spirit of competition has been built up between the science departments of the different high schools, and of course that is most commendable. Certainly these are two very worthwhile objectives even if no others are considered.

The following tabulation shows that the annual number of contestants has remained relatively constant, although the particular schools participating have varied. For example, the high school at Westerly, Rhode Island, sent a team continuously over the entire period, and was finally successful in winning the second trophy permanently in the spring of 1935. Other high schools have entered more or less sporadically, depending upon local interest and upon the yearly alternation of chemistry and physics in the high-school curricula.

It is apparent from Table 1 that interest in the contest has been maintained well from year to year. The years 1927 and 1933, for some inexplicable reason, were

TABLE 1

SUMMARY OF THE CHEMISTRY CONTEST RESULTS

Year	*No. Contestants*	*Lowest Score (%)*	*Highest Score (%)*	*Median Score (%)*
1924	67	54.0	88.0	73.0
1925	57	34.0	91.0	53.0
1926	55	33.0	92.0	64.0
1927	39	18.0	93.0	66.0
1928	55	6.0	94.1	52.0
1929	65	16.0	93.5	54.0
1930	51	17.0	77.0	45.0
1931	54	50.6	97.8	77.0
1932	56	16.0	96.0	65.0
1933	42	40.0	91.0	69.0
1934*	74	35.0	90.0	75.0
1935*	59	30.0	90.0	60.0

* Out-of-state schools participated in these years.

lowest from the standpoint of number of contestants, there being but 39 and 42 persons taking part in the contests in those years, respectively. In 1934, however, the number of contestants increased to 74 which was the largest number for any one year during the period of the contest. As will be observed from the chart, 1934 was the first year in which high schools outside the state of Rhode Island were invited to send contestants.

The tests, when corrected, were recorded in terms of scores which subsequently were converted into percentages based on the maximum score possible for any single test. As has been previously mentioned, the questions were made up in such a manner that the personal factor was decreased to a minimum in the matter of correction, and this facilitated the task materially.

The lowest percentage rating obtained by an individual contestant was 6.0% in 1928, and this varied to as high as 54.0% for the corresponding individual in the 1931 contest. The highest ranking contestants for the different years maintained a more nearly constant percentage rating, the lowest being 77.0% for 1930 as against 97.8% in 1931. The median percentage rating also showed a relatively lower variation than that exhibited by the low ranking individuals in each contest. The lowest median per cent. was 45.0% in 1930 as against the highest median value of 77.0% in 1931. These interesting and important facts are shown graphically in Figure 2.

When the number of contestants taking part in the contest each year is plotted against the years as in Figure 2, there is indicated a recurrence of interest in the contest about every three years. Just why this should be so is not easy to explain, since there are so many different factors which enter into the situation. For example, as is well known, teachers are almost never fortunate enough to have continually classes of high-grade students year after year. Then, too, it was found for other reasons to be inadvisable for some schools to participate each year. The low points of the curve appear in 1928, 1930, and 1933 and the high points in 1929, 1932, and 1935.

In Figure 3 are plotted the lowest, highest, and median percentage ratings for the different years. It seemed advisable to plot these all in one graph in order to have a common basis of comparison.

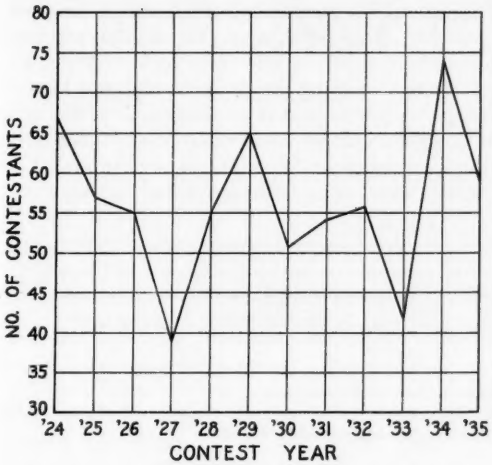


FIGURE 2.—NUMBER OF CONTESTANTS EACH YEAR

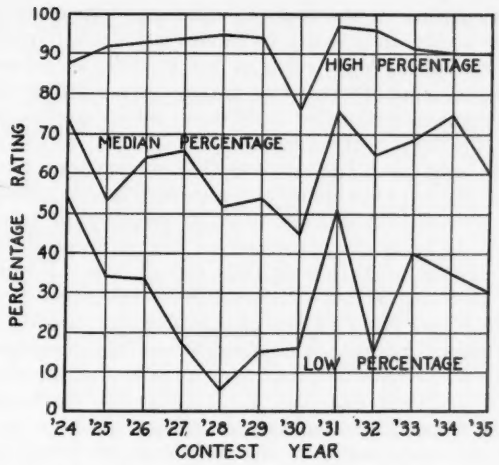


FIGURE 3.—PERCENTAGE RATINGS BY YEARS

The data indicate that there is more constancy shown in the work of the better class of students than in the case of those who ranked consistently low in the different groups. This is not unexpected inasmuch as the attempt was made, so far as possible, to choose only the high-ranking students to participate each year in the contest.

At the other end of the ranking scale, however, it is observed that the high-ranking students maintained more or less constantly a rating above 75.0%, the lowest for the whole group of contestants being 77.0% in 1930. Again this is not surprising, since it would be anticipated that those students selected for the contest in any one year would naturally be those who were in the upper one-fourth of the class. Aside from the one "break" in the curve at this point, the ratings of the high-ranking students throughout the whole period of the contests remained practically constant, in the neighborhood of 90.0%.

It was desirable and necessary, of course, that some of the question material be varied, but, on the other hand, many of the questions remained similar from year to year. Regardless of the schools or individuals competing, certain types of material and certain specific topics seemed to provide much greater difficulty for the contestants than did others. In the table which follows are tabulated the ten highest ranking topics involving question material, ranked in the order of decreasing difficulty, as indicated by the number of times the questions covering those topics were wrongly answered by the contestants.

It should be understood, however, that no attempt is made herein to distinguish between arithmetical errors, which were responsible for a problem being answered wrongly, and a person's inability to begin the solution of a problem. In either case the problem was considered to be entirely incorrect unless the right answer was obtained and the method by which it was solved was correct. and hence no credit was given for it.

TABLE 2

COMPOSITE TABLE SHOWING TYPES OF QUESTION MATERIAL ANSWERED WRONGLY WITH GREATEST FREQUENCY

Order of Frequency (Rank)	*Question Material*
1	*Gases and gas problems—converting to standard conditions
2	*Valence
3	Decomposition reactions
4	*Weight-calculation problems
5	Oxidation reactions
6	Determination of formulas from problem data as given
7	*Calculation of weights necessary for molar and normal solutions
8	Calculation of percentage of water of hydration in a compound
9	*Facts relating to industrial processes
10	*Names and correct formulas of compounds

* Topics appeared every year.

The foregoing tabulation brings out two significant facts. Apparently those topics which necessarily involve much theory and demand the exercise of considerable imagination are difficult for high-school students. Two such topics are the study of gases and their behavior and the application of valence. Topics of this kind are much harder for the secondary-school pupil than those such as Nos. 9 and 10, wherein memorization of data and the acquisition of factual knowledge are more essential than the use of imagination and the consideration of much theory. Why should this be so?

It is not surprising, inasmuch as those topics which seem difficult for the student require a power of reasoning and an ability to think independently. How frequently the complaint is made that students know facts but are unable to draw generalizations and proper conclusions and to think through a problem which differs only slightly in statement from the material which has been so carefully memorized from the textbook. Reasoning ability is very seldom inborn in an individual and is but slowly acquired.

Of the ten topics listed in Table 2, six have appeared in every test that has been given. One reason for this is the fact that each year those same types of topics have seemed to provide much difficulty for the students

participating in the contest. Students have consistently shown an inability to handle satisfactorily problems involving conversion of gas volumes calculated under one set of conditions to the corresponding volumes calculated under a different set of conditions. What is the probable reason? The difficulty is not too frequently one of a mathematical nature, but more often is due to the inability of a student to reason sufficiently well to enable him to set up properly the necessary mathematical statement of the problem before proceeding with the required calculations. Despite the fact that many of the teachers anticipated from year to year certain types of questions that would undoubtedly appear on the examinations and, moreover, were sent copies of previous tests (thereby affording their students the possibility of special coaching), there appears unmistakable evidence that there were certain fundamental topics in which every student found considerable difficulty.

Valence necessitates imaginative effort. This is true of the teacher as well as of the learner. It is an intangible though very necessary concept in the field of chemistry. To visualize properly the application of valence is difficult for college-trained persons, and hence it is not at all unexpected that in his first encounter with the topic of valence in high school, the average high-school student would not at all grasp the meaning or the application of the subject of valence.

Again, in the handling of weight-calculation problems, the arithmetic is really of secondary importance, inasmuch as the proper solution of such a problem depends upon two factors: first, the correctness of the equation involved, and second, the proper reasoning necessary for the set-up of the proportionality demanded for the solution of the problem. Unless a student is able to reason out these matters, he will find difficulty in making any progress in the solution of problems of this kind.

The calculation of weights required for molar and normal solutions seems to cause less trouble than any of the foregoing topics. In fact, the only difficulty in this connection comes from a lack of proper understanding of the term hydrogen-equivalent. Once this is understood by the student, there is usually not much difficulty encountered with this sort of problem.

Students in general, whether in high school or in college, always find it easier to learn and retain facts relating to industry and industrial processes than to think through a problem to its logical conclusion. To many persons, thinking independently is a difficult procedure, and certainly nothing demands more independent thought than does reasoning as applied to the solution of chemical problems. Memorization of descriptive matter is not hard, requiring as it does the exercise of little or no original thinking; and for that reason, questions of that sort are usually well answered. From the teacher's point of view it is more difficult to evaluate properly a descriptive question than it is to judge a question which demands the application of the reasoning process.

What about the reactions of high-school teachers to this contest? In general, it may be said that practically all high-school teachers who have had anything to do with it seem to feel favorably inclined toward its continuance. A few appeared to disagree as to the actual value of such a contest, contending that it does not accomplish the purpose for which it was intended, and still others seem to be little interested one way or the other.

It is of interest and much worth while to note briefly one or two comments which have come to the attention of the chemistry department concerning the contest. One teacher makes the following statements:

> "..... was felt that a part of the test was a test of mental alertness rather than chemistry....."
> "Regarding the true-false section, they (the students) feel that this is a satisfactory type for one part."

Another teacher writes in a somewhat different vein,

> "..... May 12 is too early from the standpoint of normal completion of the first-year course, plus a little time for an intensive review for the 'chemistry team'."
> "Relative degree of difficulty is good. I think it is a good sampling of questions on a first-year course."
> "A contest of this kind can be used to help a curricular subject. Pupils like competition and this is a movement in the right direction. We should have more interschool competition in academics. We are top-heavy in athletics."

Space does not permit the quoting of a number of other similar statements which convey a rather good idea of how teachers felt about the contest. It seems, however, that one teacher in particular does sum up the whole situation splendidly in these words:

> "..... these contests have certainly contributed to extending an appreciation of chemistry through the schools of Rhode Island and have been an undoubted factor in motivating earnest study on the part of a considerable number of boys and girls."

What, then, about the contest from the point of view of the college department which has been conducting it? It has been felt that the results have justified its continuance throughout the twelve years. In practically every instance of a high-school student's taking the examination and doing well in it, that student has achieved an enviable record in his subsequent work in chemistry. Many of the contestants have attended Rhode Island State College after graduation from high school. Some have gone to other institutions of higher learning. Wherever they have gone, it has been generally true that their subsequent study in chemistry has been of high caliber.

It is felt that the contest series provides a most excellent means of showing to the student that there may well be effective competition in an academic subject as well as in athletics. This, it would seem, might be considered as one of the most valuable outcomes of the contests.

Copies of the tests employed will be supplied by the authors upon request.

CRYSTAL CHEMISTRY

II. THE STRUCTURES OF BINARY COMPOUNDS. POLARIZATION. THE IONIC AND COVALENT BONDS

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THE polarization, or distortion, of atoms and ions exerts a strong influence upon the structure of ionic crystals; and as a preface to the general discussion of the structure of binary compounds, it is well to consider, at some length, polarization and its influence upon the nature of the chemical bond in crystals. We shall also attempt to answer, in so far as it is now possible to do so, the following questions: Are the ionic and covalent bonds different in kind, or does the covalent bond represent an extreme polarization of the ionic bond? How may the ionic or covalent bond be identified? What is the relation between crystal structure and bond type?*

First, let us review and summarize briefly, certain important facts concerning ions:

1. In comparison with the number of positive ions known, the number of negative ions is very limited. Probably only the following simple ones exist: H^-, F^-, Cl^-, Br^-, I^-, $O^=$, $S^=$, $Se^=$, $Te^=$.

2. These negative ions are all characterized by the rare gas configuration—two or eight electrons in the outer shell.

3. With anions of similar structure (*e.g.*, Cl^- and $S^=$), the radius and the polarizability increase with the nuclear charge; with cations of similar structure (*e.g.*, K^+ and Ca^{++}) the reverse is the case.

4. The number of anions is limited further by polarization; for, as we shall see later, strong polarization leads to a non-ionic or covalent bond, thus eliminating the ion as such.

5. Reference will be made in the following discussion to five types of ions, classified according to structure;

(*a*) Those with two electrons in the outer shell: H^- and the cations of the first period.

(*b*) Those with eight electrons in the outer shell: the negative ions and those of the A sub-groups of the periodic table, not including the transition elements. The eight-electron ions will be referred to as A-cations.

(*c*) Ions of the transition elements, containing eight to eighteen electrons in the outer shell.

(*d*) The ions of the B sub-groups, containing eighteen electrons in the outer shell and referred to hereafter as the B-cations.

(*e*) A few ions of the B sub-groups which are stable with 18 + 2 electrons in the outer shell will be referred to as the B + 2 cations.

* For an extremely interesting and useful account of the development of electronic theories of the ionic and covalent bonds, the reader is referred to a recent paper by WILLIAM A. NOYES, *Chem. Rev.*, **17**, 1–26 (1935).

THE IONIC BOND (*4*, *5*)

The formation of an ionic compound is influenced principally by two factors: (1) the ability of the metal atom to deliver one or more electrons, and (2) the affinity of the non-metallic atom toward electrons. The ions in a solid crystal are held in equilibrium by the attractive force of the oppositely charged ions—the coulomb force—and by the repulsive force of the negative electron clouds of adjacent ions. A measure of the first factor is the so-called ionization potential of the atom, the energy required to remove one or more electrons from the atom. These ionization potentials may be determined very accurately from spectroscopic data and have been so determined by a number of investigators. A partial list, from a recent collection (*4*) is given in Table 2. The values in column one, expressed in volts, are the energies required to remove the first electron; as would be expected, more energy is required to remove two or more electrons, and these energies are given in the other columns. For the complete table the original paper should be consulted.

TABLE 2

IONIZATION POTENTIALS OF SOME COMMON ATOMS

No. of Electrons Removed / *Atom*	*At. No.*	*1*	*2*	*3*	*4*	*5*	*6*
Li	3	5.368	75.282	121.86			
Be	4	9.281	18.14	153.10	216.8		
B	5	8.33	23.98	37.75	258.1		
C	6	11.217	24.28	47.7	64.2	389.9	487
N	7	14.48	29.47	47.17	(73.5)	97.42	(546)
O	8	13.55	34.93	54.88	77.0	109.2	137.48
F	9	18.6	34.6				

Atom	*Electrons Removed* 1	2	*Atom*	*Electrons Removed* 2	*Atom*	*Electrons Removed* 3	4
Li	5.368	75.3	Be	18.14	C		64.19
Na	5.116	47.0	Mg	14.97	Si	33.30	44.95
K	4.321	31.7	Ca	11.82	Ge	31.97	45.50
Rb	4.159	(16)	Sr	10.98	Sn	30.49	40.57
Cs	3.877		Ba	9.95	Pb	31.91	43.95
Cu	7.69	20.2	Zn	17.89	Ti	27.6	44.66
Ag	7.53	17.0	Cd	16.84	Zr	24.0	33.83
Au	9.19		Hg	18.67			

The data lend support to many ideas which the elementary student gains from the periodic table. Cesium gives up one electron more easily than any other element; it is the most positive of the elements and has the greatest tendency to form an ionic bond. The elements of the B sub-group (copper, silver, and gold) do not lose an electron as easily as do the alkali metals; they are less positive. But they can lose a second electron more readily than can the alkali atoms—hence the

prevalence of divalent copper ion, and the non-existence of divalent sodium or potassium ions. The percentage difference in ionization potentials between the A and B sub-groups is less in Group II than in Group I and, as is to be expected, has almost vanished in Group IV. It is quite evident that the quadrivalent ions of Group IV are difficult to form, but that the trivalent ions of the A sub-group (Ti and Zr) are apparently formed much more readily. This is consistent with the chemical behavior of these elements. *Evidently the third- and fourth-group elements do not have a strong tendency to form the ionic bond.*

Ionization potentials have recently been calculated theoretically upon the basis of quantum mechanics (*6*), and are found to agree with these experimental values.

Sherman (*4*) has also calculated the electron affinities of the common, negative-ion-forming elements, and his average values are given in Table 3.

TABLE 3

ELECTRON AFFINITIES OF THE ATOMS WHICH FORM NEGATIVE IONS

Energy to attach 1 electron		*Energy to attach 2 electrons*	
F	98.5	O	−168
Cl	92.5	S	− 79.4
Br	87.1	Se	− 97
I	79.2		

The negative values for O, S, Se signify that the process is endothermic. The first electron attaches itself to the neutral atom with comparative ease, but to attach the second one considerable work must be done to overcome the repulsion of this electron by the negative ion. These values are calculated by the use of the so-called Born-Haber cycle (*7*, *8*).

$$\begin{array}{ccc} [MX] & \xrightarrow{+\,U_{MX}} & (M)^+ + (X)^- \\ -Q_{MX}\uparrow & & \downarrow -I_M + E_X \\ [M] + \tfrac{1}{2}(X_2) & \xleftarrow[-S_M\ -\frac{1}{2}D_{X_2}]{} & (M) + (X) \end{array}$$

The steps represented are, from the upper left-hand corner:

1. The crystal MX is dispersed into gaseous ions.
2. The ions are converted into monatomic (neutral) gases.
3. The elements, as monatomic gases, are converted into their standard states at 25°C. and atmospheric pressure.
4. The elements in their standard states are combined to form the crystal.

U = lattice energy of the crystal.
Q = chemical heat of formation.
S = heat of sublimation.
D = heat of dissociation.
I = ionization potential.
E = electron affinity.

Evidently, any one of these quantities may be calculated when all the others are known (*4*, *9*). Recently Born and Mayer (*10*) have derived a new equation for the crystal energy, in which the van der Waals attraction between adjacent negative ions is taken into account. We shall see later that the lattice energy is a characteristic property of an ionic crystal. The nature of the bond in the crystal may sometimes be judged by a comparison of the experimental and theoretical values for lattice energies, calculated on the assumption that the crystal is ionic.

POLARIZATION. METHODS OF MEASURING POLARIZATION

In an earlier paper (*1a*), the following rules governing polarization were stated arbitrarily.

1. For a series of ions of the same charge, the smaller the ionic radius, the greater the polarizing effect of the ion.
2. For ions of the same size, the greater the nuclear charge, the greater the polarizing effect.
3. The larger the negative ion, the more easily it may be polarized.

The methods used for obtaining some of the specific data which support these statements will be considered in greater detail.

Molecular Refraction

If an atom is placed between the positive and negative poles of a condenser, the positive nucleus is attracted toward the negative pole, and the negative electron cloud is attracted toward the positive pole. The ion is then distorted or, strictly speaking, is polarized. The polarization (α) consists in the formation of a dipole; the magnitude of its effect is the product of one of the charges (e) and the distance (l) separating them, and it is proportional to the intensity of the field (I); or $\alpha = el/I$.

It was shown some time ago (*11*) that according to the electromagnetic theory of light, atoms and ions will be polarized in like manner by the electric field of light waves. They then refract the light according to the Lorentz-Lorenz equation:

$$R = \frac{n^2 - 1}{n^2 + 1} \cdot \frac{M}{d}$$

where R = molecular refractivity
M = molecular weight
d = density of the substance
n = refractive index

The polarizability (α) of a particle is proportional to its molecular refractivity, as expressed by:

$$\alpha = \frac{3R}{4N}$$

where N = the number of molecules in a gram molecule
$= 6.06 \times 10^{23}$.

For any substance n and d may be measured, and from these the polarizability may be calculated.

The polarization of atoms and ions has been studied by means of refractivity measurements by Wasastjerna (*12*) and Fajans and Joos (*13*). Figure 2 (*14*) shows the molecular refractivities of the rare gases and the ions with the rare-gas configuration. It is evident from these data that: (1) in the series Ne, A, Kr, Xe, or Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, the refractivity, and thus the polarizability, increases with increase in atomic number,

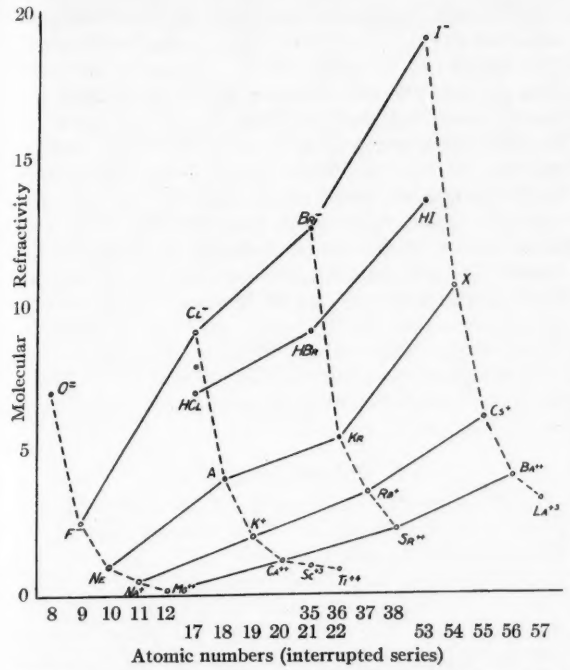

FIGURE 2.—REFRACTIVITIES OF GASES AND GASEOUS IONS (FAJANS)

and therefore with increase in the size of the atom or ion; (2) in a series of ions of similar electronic structure, like $O^=$, F^-, Ne, Na^+, Mg^{++}, there is, again, an increase in the polarizability with increasing ionic size. All of these ions have the neon structure, but the increase in atomic number from $O^=$ to Mg^{++} means that the effective radius of Mg^{++} will be less than that of $O^=$. The magnitude of the effect of a change in nuclear charge, on atoms where the number of electrons is the same is of the utmost practical importance. The refractivity may be quadrupled, for example, in going from K^+ to Cl^-. This means that, in considering polarization effects in ionic crystals, the polarizability of the cation may usually be disregarded.

When we come to refraction in binary compounds, the matter is not quite so simple as for the free ions, inasmuch as the interaction of anions and cations may be expected to have considerable influence. Let us assume, first, that the ions do not influence each other; we should then expect the refractivity of a compound to be the sum of the refractivities of the free ions, and the refractivity of the fluoride ion, for example, should be the same in all the alkali fluorides. That this is not true is shown by the data in Table 4 (*15*).

TABLE 4

POLARIZABILITIES OF THE HALIDE IONS

$\alpha \cdot 10^{24}$ for	F^-	Cl^-	Br^-	I^-
from Li salt	0.848	2.84	3.90	6.02
from Na salt	0.97	3.05	4.16	6.20
from K salt	1.15	3.25	4.45	6.61

The variation has an interesting significance. One must remember that the refraction is evidence of the polarization of an ion, produced by the passage of light and that it will be most difficult to polarize further an ion which is already deformed. That is, deformation by the light is smallest for that ion already most highly deformed; and the refraction by a deformed ion is smaller than that by one not deformed. It follows, then, that the halogens of the lithium salts must be more strongly deformed or polarized than the halogens of the potassium salts. This, of course, is consistent with the conception that the smaller of two cations exerts a stronger polarizing effect.*

The amount of deformation which one ion produces in another may also be observed by comparing the sum of the refraction of the free ions (as determined in dilute solution by Fajans and Joos) with the refraction of these ions in a crystal. The differences for the alkali halides and the alkaline earth oxides are given in Table 5 (*16*). The refractivity of the crystal is usually less than the sum of the refractivities of the free ions, indicating that the ions in the crystal do restrict each other; the smaller (and more strongly polarizing) the cation and the larger (and more easily polarized) the anion, the greater will be the decrease in the crystalline refractivity. In other words, if the anion is polarized in the crystal by a cation, its further polarizability under the external influence of light is diminished. A very small anion makes the cation more polarizable by drawing the outer electrons farther away from the nucleus and then, as in the case of KF, CsF and RbF, the crystal refractivity is actually larger than the sum of the gas refractivities. This effect is more marked in the divalent oxides.

TABLE 5

REFRACTIVE POWERS OF IONS, AS GASES AND IN CRYSTALS

		F	Cl	Br	I
Li	R (gas)	2.70	9.20	12.87	19.44
	R (cryst.)	2.34	7.59	10.56	15.98
	Diff.	−0.36	−1.61	−2.31	−3.46
Na		3.00	9.50	13.17	19.74
		3.02	8.52	11.56	17.07
		+0.02	−0.98	−1.61	−2.67
K		4.73	11.23	14.90	21.47
		5.16	10.85	13.98	19.75
		+0.43	−0.38	−0.92	−1.72
Rb		6.08	12.58	16.25	22.82
		6.74	12.55	15.78	21.71
		+0.66	−0.03	−0.47	−1.11
Cs		8.74			
		9.51			
		+0.77			

	BeO	MgO	CaO	SrO	BaO
R (gas)	7.1	7.3	8.3	9.2	11.3
R (cryst.)	3.3	4.5	7.4	9.4	12.6
	−3.8	−2.8	−0.9	+0.2	+1.3

* PAULING, *J. Am. Chem. Soc.*, **50**, 1036 (1928), has shown that departure from additivity of ionic distances and lack of consistency of other properties of the alkali halides may be related entirely to a radius-ratio effect and are not necessarily results of deformation of the ions.

The greatest variations in refractivity are to be found in a series in which very marked differences in polarization effects may occur. Several such series are shown in Table 6 (*17*). The values for the molar refractivities of the free ions are those determined experimentally in dilute solutions (*13*). Since decreasing refractivity indicates greater deformation of the anion in the crystal, fair estimates of the comparative polarizing powers of the several cations may be gained from these data.

TABLE 6

VARIATIONS IN MOLECULAR REFRACTIVITY WITH POLARIZATION

$\alpha \cdot 10^{24}$ for	Cl^-		F^-		O^-
Free Cl^-	9.00	Free F^-	2.50	Free O^-	7.0
In $SiCl_4$	7.01	In MgF_2	2.28	In TiO_2	6.2
		SF_6	1.94	CaO	6.1
				MgO	4.2
				BeO	3.2

Series Spectra

Born and Heisenberg (*18*) have determined the polarizabilities of noble gas ions from the series spectra of these atoms. Their values agree well with those calculated from refractivity measurements. Recently Mayer and Mayer (*19*) have calculated polarizabilities of ions from spectra, using the Born-Heisenberg method with certain corrections. The polarizabilities of ions of the noble gas configuration determined by these several methods are summarized in Table 7 (*19*).

TABLE 7

POLARIZABILITIES OF THE GASEOUS IONS $\times 10^{24}$ IN CM.^{3}

Ion	*M and M*	*Pauling (20)*	*F and J*	*B and H*
He		0.204		
Li	0.025	0.0295	0.079	0.075
Be	0.007	0.0080	0.039	
B	0.0033	0.00303		
C	0.0015	0.00135		
Ne		0.396		
Na	0.17	0.182	0.197	0.21
Mg	0.10	0.092	0.110	0.12
Al	0.053	0.054		0.065
Ar		1.645		
K	0.80	0.844	0.879	0.87
Ca	0.54	0.474	0.447	
Kr		2.49		
Rb	1.5 (?)	1.42	1.485	1.81
Sr	1.0	0.87	0.883	1.42
Xe		4.05		
Cs	2.35	2.45	2.577	2.79

Goldschmidt has calculated the fields of the cations, measured by the (ionic charge)/(ionic radius)^2, to give some idea of the polarizing powers of the cations. His results are given in Table 8 (*21*), and compared with values for the halide ions. It is evident that, the smaller the cation, the greater its polarizing power; and that as a rule, the polarizing power of anions is negligible.

TABLE 8

POLARIZING POWER OF CERTAIN CATIONS (GOLDSCHMIDT)

Li	1.7	Be	16.0					F	0.6
Na	1.0	Mg	3.3	Al	9.2	Si	26.0	Cl	0.3
K	0.6	Ca	1.8	Sc	4.4	Ti	9.8	Br	0.3
Rb	0.5	Sr	1.2	Y	2.7	Zr	5.3	I	0.2
Cs	0.4	Ba	1.0	La	2.0	Ce	3.8		
						Th	3.3		

It has been suggested that polarization is the forerunner of a change from the ionic to a semi-ionic bond. This appears to be confirmed by the data which have been given. The cations which have the smallest polarizing power are those with the lowest ionization potentials—those which favor the formation of the strongest ionic bond. The anions which resist polarization most strongly are those which have the high electron affinities; again, those which favor the formation of an ionic bond. As the electron affinity of the anion decreases, its polarizability increases, and as the ionization potential of the cation increases its polarizing power increases. Both trends produce a departure from the pure ionic bond. This brings us back again to our original premise that, as the size of the cation decreases or the size of the anion increases, polarization in the compound increases.

Ultraviolet Absorption

Another interesting method for the detection and estimation of polarization is the measurement of the absorption band in the ultra-violet (*22*). It seems that the position and state of this band are related to the degree of polarization in the lattice of the compound under consideration. The band is very sharp for fluorides and grows broader through the series F^-, Cl^-, Br^-, I^-. Through the series $Li^+ \rightarrow Cs^+$ it also becomes broader. Evidently the sharpness decreases with increasing polarization, because with increasing polarization the energy state of the ion in the crystal deviates farther from the definite free-ion value; that is, the ion is "spread out." It is noteworthy that the silver halides give no discrete absorption band, but a wide absorption region, indicative of extreme polarization in these crystals.

Interionic Distances

When the interionic distances in crystals deviate from the sum of the radii of the ions concerned it is usually taken as evidence of polarization (*14, 23*). No doubt this is the proper deduction in the case of the B-cations for which polarizing power is relatively high, but, as mentioned above, it has been demonstrated (*24*) that in the case of the alkali halides, in which little deformation is to be expected, the deviations may be due entirely to a radius-ratio effect.

Comparative Lattice Energies

The comparison of lattice energies of ionic crystals with the values calculated theoretically gives some indication of the extent of polarization in crystals (*4*). When there is every reason to suppose that the crystal is a pure ionic form, like the potassium halides or the alkali chlorides, then the calculated and observed values agree very closely. The disagreement increases as the bond becomes less ionic; that is, as polarization increases.

Wave-length of the K-absorption Edge of the Atom

There is reason to believe that the polarization in a crystal is related to the wave-length of the K-absorp-

tion edge of the atoms involved. The development of this method constitutes another chapter in that fascinating story, called by Richtmyer "The Romance of the Next Decimal Place," and reference may be made to his paper for a detailed description (*25*). This line of investigation has been developed by Stelling (*26a, b*) and others. On the other hand, it is maintained (*27, 28*) that the shift in the K-absorption wave-length can be brought about by the effect of the electrostatic action of the neighboring ions in a crystal and is not necessarily due to polarization of the ion, although the chances are that for the B-cations, polarization is a significant factor.

Certainly a careful scrutiny of available data reveals many inconsistencies, and there is some question as to how far this method of estimating polarization can be followed.

Ionic Diffusion in the Solid

Von Hevesy has suggested (*29*) that, inasmuch as polarization is a transition state between the ionic and covalent bonds, it causes a loosening of the bonds in the crystal. This loosening is manifested by the rate of ionic diffusion in the solid, the rate increasing as the ionic bond becomes more and more polarized. We shall see later that color and other characteristic properties of certain compounds may be intimately related to this "degeneration" of the ionic bond.

In brief, then, the polarization properties of atoms and ions have been calculated from refractivity data and from series spectral data. Indirectly, polarization properties may be estimated from ionization potentials and electron affinities, from ultra-violet absorption spectra, lattice energy values, interionic distances and from rates of ionic diffusion; and, perhaps, from studies of the wave-length of the K-absorption limit.

Data obtained with the help of all of these methods, direct and indirect, point to the same generalizations stated heretofore, namely:

1. For a series of cations of the same charge, the smaller the ionic radius, the greater the polarizing effect of the ion.
2. For cations of the same size, the greater the nuclear charge, the greater the polarizing effect.
3. The larger the negative ion, the more easily may it be polarized.
4. Polarizing power is least for the A-cations, most for the B-cations, and intermediate in strength for the ions with incomplete eighteen shells—the transition element ions.

THE TRANSITION FROM THE IONIC BOND TO THE COVALENT BOND

Is the bond in a crystal either definitely ionic or definitely covalent, with no intermediate type; or is the transition from one bond type to the other continuous? These questions have aroused a great deal of discussion in the last few years, and even now the answer cannot be stated dogmatically. The discussion of polarization has undoubtedly given the impression that the transition is essentially continuous.

The arguments in support of a continuous transition have been ably set forth by Fajans (*14, 30*) while Sidgwick's (*23*) approach is typical of those who believe that the change is discontinuous. It is interesting that both Fajans and Sidgwick choose much of the same data to prove the opposite sides of the question:

1. The change in properties of a series of uni- to quadrivalent halides;
2. The properties of the hydrogen halides;
3. The properties of the silver halides.

The evaluation of their discussions of these three points can be followed with considerable profit, not only because of the conclusion to be reached, but because the subject offers a beautiful example of how easy it is to interpret data in favor of a preconception.

TABLE 9

BOILING POINTS OF HALIDES OF SODIUM, SILICON, ALUMINUM AND TIN AT 760 MM.

NaF	NaCl	NaBr	NaI
1695	1441	1393	1300
SiF_4	$SiCl_4$	$SiBr_4$	SiI_4
−90	57	153	ca. 290
AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
800	183	260	350
SnF_4	$SnCl_4$	$SnBr_4$	SnI_4
705	114	203	300

In Table 9 (*31*) are listed properties which give a measure of the relative stabilities of a series of halides. It may be observed that the halides of a given element are either relatively high-boiling, the boiling points falling slowly as the atomic weight of the halogen increases; or they are low-boiling, the boiling points rising more rapidly as the atomic weight of the halogen increases. The decrease in boiling point with increasing atomic weight (and atomic size) is to be expected in ionic compounds, since the distance between the ions increases. In a series of organic compounds, on the other hand, the boiling point increases with the molecular weight. This type of variation has become associated with the existence of the covalent bond. Sidgwick, therefore, assumes the sodium halides to be typical ionic salts; while the silicon halides are taken as characteristic covalent compounds. Regarding the aluminum halides, there arises a difference of opinion. Sidgwick says that they demonstrate a discontinuous change from ionic to covalent bond; Fajans cites them as indicative of a continuous transition. It has been shown, however, that all those properties related to the stability of a compound are determined primarily by the environment of the building stones in the crystal, not by the existence of ionic or covalent forces between them (*32, 15*). In so far as this is true, all the data of Table 9 are beside the point, and have no direct bearing upon the problem.

Pauling has recently calculated, upon the basis of the quantum mechanics, that the bonds in SiF_4 are neither ionic nor covalent, but represent an average of the two extremes (*32*). There is, in fact, no reason to believe that there should be a sudden and complete change in

the type of bond in passing from $MgCl_2$ to $AlCl_3$ along the series of NaCl, $MgCl_2$, $SiCl_4$, PCl_5; and there is no evidence of such a change.

The properties of the hydrogen halides have also been called to witness for both the continuous and discontinuous transitions. HCl is difficult to solidify and forms a molecular lattice. These properties may probably be attributed to the covalent bond indirectly, although the low freezing point follows directly from the weak molecular lattice. In water, HCl is a strong electrolyte. If HCl were ionic, the distance 1.26 Å. between its nuclei would be identical with the dipole distance, determined from the dipole moment; but if HCl is covalent, the dipole distance should be zero. So reasons Fajans and concludes that, because the actual dipole distance is 0.216 Å. the bond must be of an intermediate type—a polarized ionic bond (*33*). Sidgwick, however, states arbitrarily that the covalent link has a dipole moment; that is, the electron pair is rarely shared equally by the two atoms; and cites as proof the case of HCl which he *assumes* to be entirely covalent.

Pauling interprets the calculated potential energy curves of the hydrogen halides (*32*) as indicating that H_2F_2 is of an intermediate bond type, predominantly ionic, as evidenced also by the tendency of fluorine to form hydrogen bonds; while in HCl, HBr, and HI the covalent bond makes the greater contribution.

Certain properties of the series AgF, AgCl, AgBr, and AgI have been taken to suggest the continuity of the bond transition, or its discontinuity, as one chooses. The first three crystallize in the NaCl structure, the last in the ZnS and ZnO structures. This series is cited as evidence of the discontinuity of the transition from ionic to covalent bond, when it is *assumed* that a change in structure from the NaCl to the ZnS(ZnO) lattice is proof of a change in bond type, an assumption which is not justified. On the contrary, this series of salts proves to be one of the most convincing exhibits in favor of the continuous transition in bond type. To mention only AgI, while it does crystallize in a form usually associated with the covalent bond, it has a slight tendency to ionize in water and shows considerable ionic conductivity in the solid state. AgI cannot be called a covalent compound, although it may be considered to be intermediate in bond type, and more covalent than ionic. Incidentally, Pauling (*34*) has remarked that the bond type has no direct connection with the extent of ionization in water. Thus, nearly covalent HI ionizes almost completely, whereas ionic HF is only partly ionized.

Without question, the bond type in certain crystals may vary considerably from the ionic toward the covalent and vice versa. Whether or not this should be taken as evidence of a continuous transition in bond type depends upon the interpretation of the term "continuous." The quantum mechanics rationalizes the electron-pair bond by assuming that the two electrons resonate between the two atoms. The pure covalent bond exists when the electrons exchange places at the same instant, so that on an average only one electron is allotted to each atom. If the electrons do not jump at the same instant, then for the time interval when both are on the same atom, the bond is ionic and electrostatic forces and polarization become significant. The intermediate bond may be represented by a time average position of the electron pair, an average of a covalent bond component, an electrostatic component, and certain polarization forces.

Pauling has recently shown (*32, 35*) by a wave mechanical treatment that the transition from the ionic to the covalent bond may, in certain cases, be continuous, while in other cases it must be discontinuous. In the AX compounds, for example, in the sphalerite and wurtzite structures, it is possible to have either the ionic or the covalent extreme, *or any average state between these extremes*. Certain properties of the substances in question must be considered in order to decide which type is more nearly approached.

The foregoing statement is, in fact, a most concise and complete summary of the entire question of the nature of the transition between ionic and covalent bond. It leads to the problem of the determination of the predominant bond type in any given crystal.

IDENTIFICATION OF THE IONIC BOND AND THE COVALENT BOND

A number of methods commonly used as criteria of bond type have already been mentioned. These, and others, may be summarized as follows.

Direct Methods

(1) Prediction from quantum mechanics.
   - (*a*) Directional bonds.
   - (*b*) Paramagnetic susceptibilities.

(2) Photodissociation of molecules.

Indirect Methods

(3) Agreement or non-agreement with the rules governing the structure of ionic compounds.
(4) Lattice energies.
(5) Interatomic (-ionic) distances.
(6) Crystal structure.
(7) Polarization properties, as influenced by ionization potentials, electron affinity, valence, ionic radii.
(8) Comparison of properties with properties of crystals of known bond type.

1. The nature of the chemical bond, as revealed by a quantum mechanical treatment, has been developed by Pauling (*32, 34, 35, 36, 37*) and by Slater (*38a, b*). Pauling has been concerned chiefly with the conditions favoring the formation of the covalent bond. Over the entire realm of chemical compounds, organic and inorganic, the covalent bond predominates, while there exists a relatively small percentage of ionic compounds. In a discussion limited to the inorganic binary compounds, one is apt to acquire an exaggerated idea of the importance of the ionic bond.

When only *s* electrons are available, having spherical orbits with no directional properties, the bond formed

is usually ionic. When *s* and *p* orbitals are available, it has been shown that an atom can form four or fewer equivalent bonds directed toward the corners of a tetrahedron (bond angles 109° 28′). In bivalent nickel, palladium, and platinum, containing eight *d* electrons in the outer sub-shell, four strong bond orbitals can be formed, lying in a plane and directed toward the corners of a square. When six or fewer *d* electrons are present, six d^2sp^3 orbitals will be formed, directed toward octahedral corners. This type of bond is formed in many complexes such as $(PtCl_6)^=$, $Fe(CN)_6^{-3}$, and others. With more than six *d* electrons, six bonds are formed directed toward the corners of a trigonal prism of unit axial ratio.

It is evident, then, that crystal structure determinations which establish the direction of chemical bonds will throw considerable light on the nature of these bonds. While it is true that the tetrahedral and octahedral bonds may be either ionic or covalent,* the square and trigonal prism bonds are not stable configurations for ions, and their existence is therefore good evidence of the covalent bond. The bonds in K_2PdCl_4 and K_2PtCl_4 may be considered as covalent on this basis.

Pauling has shown that when the ionic and covalent structures of a compound have different multiplicities† the type of bond may be determined from the paramagnetic susceptibilities. The expected magnetic moments for the ionic and covalent bonds are 5.91 and 1.73 Bohr magnetons respectively. When the experimental values, calculated from the measured paramagnetic susceptibilities, are: $(NH_4)_3FeF_6$ = 5.88, $FeCl_3$ = 5.84, $FeSO_4 \cdot 7H_2O$ = 4.99, FeI_3 = 5.4, $K_3Fe(CN)_6$ = 2.0, it may be said with reasonable certainty that the bonds are essentially ionic in the first four compounds and covalent in the last. Note that from general knowledge of the influence of polarization upon bond type one would predict an ionic bond in $(NH_4)_3FeF_6$ and a covalent bond in $K_3Fe(CN)_6$ since the fluoride ion is not easily polarized, while it is to be expected that the unsymmetrical cyanide ion is subject to strong polarization.

2. The molecules for which photodissociation has been studied may be divided into two distinct groups: When a molecule dissociates into two neutral atoms, one excited, the covalent bond is indicated. Among these may be listed Cl_2, Br_2, I_2, H_2, S_2. When two neutral atoms, both excited, are formed, the ionic bond is indicated, as in NaCl, NaI, KBr, RbBr and others (*39*, *40*).

When the multiplicity of a complex is the same for both ionic bonds and covalent bonds, then indirect evidence must be relied upon to suggest which of the two types is more nearly approached. The remaining six criteria listed above are of this indirect type.

3. When the arrangement in a crystal is tetrahedral, if the bonds are covalent, angles of 90° or 109° are to be expected; while ionic bonds would permit larger angles. Hence the angle of 180° in *beta* tridymite indicates bonds largely ionic (*35*). When the shared octahedral edges are shortened, as in hematite and corundum, an ionic bond is suggested; while the longer, shared octahedral edges in marcasite indicate a covalent bond. In MoS_2, the sulfur atoms are at the corners of a trigonal prism around the molybdenum, not at the corners of an octahedron, and covalent bonds are therefore indicated.

4. The interpretation of lattice energies as they indicate bond type has already been discussed in some detail (*4*, *8*).

5. Altogether too much stress is placed upon the importance of interatomic distances as criteria of bond type. Considerable significance has been attributed to the fact that in the ZnS lattice the interatomic (ionic) distance is some 5–8% less than for the same atoms arranged in a NaCl lattice. Goldschmidt first established this relationship. Let us examine data for the silver halides, as shown in Table 10, from this point of view.

TABLE 10

INTERATOMIC DISTANCES IN THE SILVER HALIDES IN Å

	AgF	AgCl	AgBr	AgI
Sum of ionic radii (C.N. = 6)	2.46	2.94	3.09	3.33
Experimental distances	2.46	2.77	2.87	3.05*
Difference		0.17	0.22	0.28
Per cent. decrease		5.8	7.1	8.4
Sum of ionic radii (corrected to C.N. = 4)				3.14
Experimental distance				2.811
Difference				0.33
Per cent. decrease				10.5

* For Ag-I in AgI of NaCl structure, calculated from mixed crystals of AgI-AgBr.

As evidence of the covalent bond in silver iodide, it is frequently pointed out (cf. Sidgwick, "The Covalent Link") that there is a contraction of 9% in the interatomic distance in *beta*-AgI (2.81 Å.) as compared with the interionic distance in an "ionic" (NaCl) lattice (3.05 Å.). In citing this evidence two facts have been overlooked, either one of which is sufficient to make the evidence worthless for its purpose. First, a large fraction of this contraction may be due to a radius-ratio effect or to a change in coördination number and is entirely independent of the influence of the type of bond. Zachariasen has calculated (*41*) the effect of coördination number on *ionic* radii and his results show that the magnitude of the contraction when the coördination number changes from six to four is about that determined by Goldschmidt from the comparison of experimental values—about 4–5%. Furthermore, the contraction in the atomic radius of tin in the transition, white tin (C.N.= 6) to grey tin (C.N.= 4), is about 7% (*42*).

In both these instances it must be emphasized that the change in interatomic distance is due to a change in coördination number, *not in bond type* (the metallic and covalent bonds are generally conceded to be commensurable). If we assume, then, that merely the decrease in C.N. from 6 to 4 will cause a contraction of

* Note that the tetrahedral or diamond structure is not conclusive evidence of covalent bonds, although it is frequently assumed to be so.

† Different numbers of unpaired electrons.

about 5.5% in interatomic distance, the theoretical AgI distance (C.N.= 4) will be $3.33 \times 0.945 = 3.14$ Å., as compared with the experimental distance 2.81 Å. The per cent. contraction of the observed distance is, therefore 10.5%, which is not out of line with 8.4% contraction for AgI and 7.0% for AgBr in the "ionic" (NaCl) lattice, assumed to be due to polarization. The point is, in short, that when the strong contraction of 3.05 Å. to 2.81 Å. in the Ag-I distance is attributed to a change in bond type, it is a misrepresentation of the facts, since a contraction from 3.04 to 2.88 (3.05×0.945) is to be expected solely as a result of the decrease in coördination number and entirely apart from the influence of the type of bond. The value 2.88 Å. for the Ag-I distance then represents the interionic distance corrected for a change in coördination number from 6 to 4 and for the increase in polarization effect resulting from the substitution of iodide for bromide. It is evident that there is not much left (2.88–2.81) of the large contraction supposedly due to a change in bond type, and much of the remaining difference can readily be attributed to the increase in polarization to be expected because each silver ion can concentrate its polarizing influence on four iodide ions instead of six.

The truth of the matter is that the deviations of the interionic distances in the silver halides offer excellent proof of a continuously increasing polarization of the ionic bond, and there is no discontinuity in interionic distances to suggest that a pure covalent bond comes into existence—gradually or suddenly. Sight must not be lost, however, of the fact that, as is nicely illustrated by these data, the interionic distance is very useful in suggesting a trend from the ionic toward the covalent bond in the direction of AgF to AgI.

The covalent bond is often assumed to be present when the interatomic distances in crystals agree more closely with the sum of the atomic radii than with the sum of the ionic radii (see, *e. g.*, Sidgwick, "The Covalent Link"). One need only follow through with this criterion to lose faith in it. Too often, when the apparent agreement of the observed distance and the sum of the radii is cited as evidence of the covalent bond, the correction of the calculated radii for coördination number has been neglected. When the correction is made, as for AgI, above, it is evident that there is no longer any significant agreement between observed and calculated distances.

There is, however, one respect in which interatomic distances seem to be an indication of the presence of the covalent bond. It has been found that, in a series of compounds with the wurtzite or zincblende structure, in which the element A stands as many places before the fourth group as the element X stands after the fourth group, the interatomic distances are essentially constant. Several such series are shown in Table 11A. Now, it is well known that in ionic crystals of the same sort (see Table 11B), the interionic distance decreases as the valence of the ions increases. The fact that there is no such decrease in the wurtzite or zincblende structures with increasing valence suggests very strongly that these crystals are not built of ions, but of atoms. In short, the interatomic distance seems to depend upon the total number of electrons, not on their distribution between the atoms.†

TABLE 11

A. Distances between particles in zincblende-wurtzite structures		B. Distances between particles in NaCl structure (ionic lattice)	
AgI	2.811	NaF	2.310
CdTe	2.799	MgO	2.104
InSb	2.793		
SnSn	2.79	KF	2.669
		CaO	2.401
CuBr	2.460		
ZnSe	2.452	RbF	2.815
GaAs	2.435	SrO	2.573
GeGe	2.43		
		NaCl	2.614
CuI	2.618	MgS	2.595
ZnTe	2.637		
GaSb	2.638	KCl	3.139
Ge + Sn	2.62*	CaS	2.843
SeCd	2.62	RbCl	3.286
		SrS	3.004
CuCl	2.341		
ZnS	2.346	NaBr	2.981
GaP	2.354	MgSe	2.726
Ge + Si	2.39*		
		KBr	3.293
AsAl	2.437	CaSe	2.956
MgTe	2.76	RbBr	3.434
AlSb	2.638	SrSe	3.113
Si + Sn	2.57*		
		KI	3.525
SCd	2.521	CaTe	3.172
AlP	2.360	RbI	3.663
SiSi	2.347	SrTe	3.324
AlN	1.87		
SiC	1.89		
BeO	1.645		
CC	1.541		
BN	layer structure		

* These values are calculated, since the actual crystals are not known, and are the sums of the atomic radii.

6. It must now be apparent that the type of bond in a given compound cannot be predicted with certainty from its crystal structure. It is equally true, however, that the crystal structure may be very suggestive of the bond type. Thus, the NaCl structure does not permit the formation of a covalent bond, since there are too many neighbors around a sodium atom to permit each one to be held by a pair of electrons. It may be possible, however, for electron pairs to jump from one atom to another, forming more bonds than there are electron pairs. Probably ScN is covalent in spite of its NaCl structure. This is suggested on two counts:

(*a*) its valence and ionization potential are high (see 7*c*, below);

(*b*) its properties are similar to those of diamond, a typical covalent crystal.

On the other hand, the zincblende or wurtzite structure does not guarantee the existence of a covalent bond. It has been shown that in AgI the bond is, at best, of an intermediate nature and retains some ionic

† On the contrary, see data on hardness, and comment thereon. in a later instalment.

characteristics. BeO is essentially ionic (*30*, *43*) as is NH_4F; and the sulfide, telluride and selenide, of beryllium may also be largely ionic (*44*).

7. The same factors which tend to increase polarization will favor the transition from the ionic to the covalent bond. Thus, the covalent bond is suggested when:

(*a*) the ionization potential is high;
(*b*) the electron affinity is low;
(*c*) the cation is small and strongly polarizing and/or the anion is large and easily polarized;
(*d*) the valences of A and X are high. Trivalent and tetravalent AX compounds, for example, are rarely ionic.

8. It cannot be too often repeated that the stability of a compound as indicated by melting point, solubility, and so on, is no indication of the type of bond present. Ionic and covalent bonds may be of the same relative strengths. A similarity of physical properties, however, often suggests a similarity of bond. Thus, PbS, PbSe, and PbTe, although they are said to have the NaCl structure, are obviously more like FeS and FeS_2 than like CaS, and they are probably not ionic compounds.

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NOTE ON THE COMBUSTION OF METALS IN OXYGEN AND SULFUR

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IT IS often desirable to point out to beginning students similarities and differences in the behavior of two elements in the same family. This is a simple matter if both elements exist normally in the same state. In the case of oxygen and sulfur, however, the one being a gas and the other a solid, it is necessary to make the comparison in the gaseous state. This can be accomplished in the following simple manner.

An oxygen-generating mixture consisting of potassium chlorate and manganese dioxide is placed in the bottom of one hard glass test-tube and a few grams of sulfur in another. A loose wad of steel wool is placed in each tube so that it stands a short distance above the solid. The tubes are then heated, the heat being gradually extended upward to include the steel wool. Upon reaching the ignition point, the wool burns with a brilliant flash in oxygen, but is little affected by the sulfur vapor. Copper wool or fine turnings may then be substituted for the steel wool. In this case, the copper is but superficially oxidized in oxygen, but burns vigorously in sulfur vapor. Thus, the anomaly in the behavior of oxygen and sulfur toward these two metals is visually illustrated.

Other metals may be used in a somewhat similar manner by being properly suspended in the tubes. Caution should be exercised in allowing very active elements to come in direct contact with the oxygen-generating mixture.

This method of illustrating the properties and behavior of oxygen can be used in the laboratory in place of the longer method so commonly used; this consists of generating the gas in a prepared generator, collecting it over water in bottles and inserting the preheated metals or other elements in the collected gas.

EMULSION STABILITY *and* FAT EMBOLISM*

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The problem of fat embolism is discussed as the result of the breaking of the normal fat emulsion in the blood. Some preliminary experiments are reported on the breaking of comparable oil-in-water emulsions stabilized by egg albumin. The distinction is drawn between agglomeration and coalescence of such emulsion droplets, and the dusting on of an oil-soluble dye is used to determine whether actual breaking of an emulsion results.

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TO MOST medical men fat embolism is the condition which results when fat from the marrow of a fractured bone is drawn into the blood stream, carried to the lungs, and there plugs the capillaries. The symptoms of fat embolism are asphyxial and the condition can usually be distinguished from pneumonia only by post-mortem examination. These symptoms were listed fifty years ago by Park[1] as including: early pallor; somnolence; gradually increasing respiratory rate; increasing dyspnœa; weak, rapid, irregular pulse; subnormal temperature at first, but atypical; delirium and coma. In some cases the fat is forced through the lungs and is caught in the capillaries of the central nervous system, producing in from two to seven days cerebral fat embolism with symptoms somewhat similar to delirium tremens. Pulmonary fat embolism usually occurs within two days after the injury and may sometimes be thus distinguished from surgical shock, which develops more rapidly, and from true pneumonia, which develops more slowly. Medical men differ in their opinion as to the incidence of fat embolism, all the way from the man who, out of an unusually extensive experience of post-mortem examination, declares that fat embolism occurs in every case of trauma, to the majority of physicians who believe it of rare occurrence. Truth must lie between these extremes, and an interesting question presents itself as to what bodily mechanism prevents fat embolism from becoming a serious complication in a large majority of cases of trauma, or what kind of people are predisposed to serious fat embolism. It is certain that fat embolism does occur, probably in an unsuspectedly large number of cases, but the mechanism by which it arises is not clear, nor is there any known way to prevent or cure the condition.

The study of the literature and many necropsies brought Vance[2] to the conclusion that fat embolism could arise from traumas to adipose tissue including: (1) trauma to the osseous systems, such as fractures of bones, jarring of the skeleton, and orthopedic operations; (2) trauma to subcutaneous and intermuscular fat; and (3) trauma to fatty viscera. It might also arise from the intravenous injection of various oils (especially those of higher viscosity), but Vance classified as dubious etiologic factors such cases as burns, poisons, and certain "natural" causes of death such as infections, eclampsia, diabetes mellitus, and others.

The earlier work of Lehman and Moore[3] had accepted as valid a number of the etiologic factors classed by Vance as dubious. They conclude: "Trauma, therefore, is not the cause of all fat embolism, nor, as a corollary, is the free fat found in cases associated with trauma necessarily all due to the trauma itself." They point out that swelling and blood clotting will soon operate to minimize continued entrance of fat from a fractured bone, and that often the fat found in the lungs is greater in amount than could reasonably have come from the bone. They argue that the only common factor in these numerous causes is some pathological coarsening of the physiologic ultramicroscopic emulsion of fat in blood plasma.

The physiologists seem fairly agreed that ingested fat is saponified in the small intestine and that the glycerol and soap so formed pass into the intestinal wall where they react to form a neutral fat similar to, but not necessarily identical with, that ingested. The fat then appears in the chyle as a milky emulsion and as such is poured into the blood stream where it may be observed as the "blood dust," the dispersion being so great that the fat droplets exhibit Brownian movement. Very interesting is the paper by Gage and Fish[4] who showed that on starvation these droplets (called chylomicrons) are very scarce, only two or three being visible in a standard dark field, while within four hours after a fatty meal the number of chylomicrons may rise to ninety or more, and then during about six hours the count returns to the starvation level. In order to have fat thus dispersed in the aqueous blood plasma some emulsifying agent is necessary, and it was shown

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[1] PARK, R., *N. Y. Med. J.*, **40**, 177 (1884).

[2] VANCE, B. M., *Arch. Surg.*, **23**, 426 (1931).

[3] LEHMAN, E. P. AND MOORE, R. M., *Arch. Surg.*, **14**, 621 (1927).

[4] GAGE, S. H. AND FISH, P. A., *Am. J. Anat.*, **34**, 1 (1924).

by Ludlum, Taft, and Nugent[5] that the chylomicrons are protected by films of serum albumin and serum globulin. For the purposes of this problem we have in the blood stream a fine emulsion of fat protected by protein. In the normal individual the fat content of the blood may vary from 0.2 to 2 per cent., and pathological contents as high as 26 per cent. are recorded. The normal protein content of the blood is of the order of 7 per cent., while in certain edematous conditions values as low as 3 per cent. are recorded. The problem then becomes one of discovering what pathological conditions might arise sufficient to cause the coalescence of the chylomicrons into drops large enough to form emboli or plugs in the blood vessels.

For purposes of immediate transfer, it would appear wise to study the stability of emulsions containing seven per cent. egg albumin (as most comparable to serum proteins) and two per cent. of cottonseed oil. On coagulation, as by boiling, such a system forms a jelly. Since a clear liquid layer seemed desirable as a method of recognizing complete breaking, it seemed preferable to study systems containing two per cent. albumin and two per cent. oil. Such systems should be much less stable than the physiologic emulsion so that the large stability shown by them should be an index of the tremendous stability of the normal body emulsions.

EMULSION STABILITY EXPERIMENTS

Before outlining the experiments there is need to distinguish clearly between an *agglomeration* of oil droplets, such as chylomicrons into aggregates, possibly like bunches of grapes, and a *coalescence* of these grapes into a grape fruit. This distinction is sound etymologically, and agglomeration, as evidenced grossly by an accelerated creaming, can and does take place without coalescence. The test for this is an adaptation of that used by Robertson[6] for the determination of the external phase in an emulsion. After an emulsion is broken (this word is used to express the formation of a clear liquid layer containing no visible emulsion droplets) some particles of an oil-soluble dye are added. If there has been destruction of the protective sheaths, permitting coalescence of the fat, the liberated oil drops will be dyed and thus rendered readily visible. If only agglomeration has taken place, the dye particles can no more come into contact with the oil than before the breaking agent was added. It will be shown that apparently in many cases, protein may be precipitated about the oil droplets and that the sheaths may or may not be permeable to the dye. If they are permeable, the cream is colored more or less pink.

Blank runs gave confidence in the test. The dye used was Sudan III (azobenzeneazo-2-naphthol), a common stain for fat. Particles of the dye make visible extremely small droplets of fat when shaken with water alone. Some dye was shaken with albumin solution and the sol was coagulated by boiling. The addition of free oil produced no dyeing of the oil, because the albumin coated and protected the dye particles even after coagulation. Similarly an oil-in-water emulsion protected by albumin and boiled gave no coloration when dye was added, because the protein protected the oil. But if a solution of albumin be coagulated and then dye and oil be added, there is no difficulty in seeing the red drops of oil. Heating has destroyed the ability of the albumin to surround either the oil or the dye, and the presence of the albumin does not prevent dye finding, and dissolving in, oil drops. While Sudan III is insoluble in water, it is somewhat dispersed by sulfuric acid, soaps, and proteins, especially on heating. If the powder is shaken with an agglomerated emulsion, the particles may be caught mechanically within the cream, but careful examination, especially with the microscope, will reveal whether or not there are tiny drops of oil dissolving dye. If present, these are most numerous around the test-tube at the top of the liquid.

The emulsions were prepared by the "Continental" method, studied by Briggs.[7] Very satisfactory emulsions were obtained in which most of the oil droplets were five microns or less in diameter. Such droplets show Brownian movement. Two grams of dried egg albumin was ground in a mortar, 2 cc. of cottonseed oil was added with more grinding, and then water was added slowly. The first 2-3 cc. produces a very stiff, sticky jelly which, with more water and a lot of grinding, gives a cracking sound which appears to be a mark of a satisfactory emulsion nucleus. After addition of about 6 cc. of water, this sound is no longer heard, and it appears probable that further grinding produces little added dispersion. As pointed out by Briggs, fineness of the dispersing agent when ground with the oil is a most important factor. Dilution of this nucleus, with stirring, to 100 cc. completed the preparation of the stock emulsion. Such emulsions are quite stable and show only slight tendency to cream.

Samples of 5 cc. each were taken and the following reagents were added: 3 cc. 6 *N* acetic acid; 5 cc. 6 *N* acetic acid; 2 cc. concentrated nitric acid; 2 cc. 6 *N* hydrochloric acid; 2 cc. 6 *N* sodium hydroxide; 2 cc. 5% solution tannic acid; 2 cc. 5% solution of mercuric chloride; 2 cc. 5% solution copper sulfate hydrate; 2 cc. of a mixture of three volumes alcohol and one volume ether; 1 cc. 6 *N* acetic acid, followed by 2 cc. 5% solution potassium ferrocyanide, and 3 g. of solid ammonium sulfate.

After about two hours, clear liquid layers were visible in all tubes except those containing acetic acid only, which did not clear completely. The volume of each system was diluted to 10 cc. with water in order to permit better separation, and some particles of dye were added with vigorous shaking. Care was taken to have plenty of dye on the top of the liquid where the

[5] LUDLUM, S. D., TAFT, A. E., AND NUGENT, B. L., *J. Phys. Chem.*, **35**, 269 (1931).

[6] ROBERTSON, T. B., *Kolloid Z.*, **7**, 7 (1910).

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free fat should accumulate. Final examination was made the next day.

The results of these tests can be generalized about as follows. (1) Certain substances produce an accelerated creaming due to an agglomeration of the oil droplets. These include hydrochloric acid, nitric acid, tannic acid, mercuric chloride, copper sulfate, and ferrocyanic acid. These substances produce complete separation of a white cream or precipitate (nitric acid gave yellow) in which there is no evidence of any contact between the oil and dye. (2) Certain substances produce agglomeration and some degree of coalescence. These include acetic acid, alcohol-ether, ammonium sulfate, and sodium hydroxide, among which the last is most powerful. Although the acetic acid did not produce complete separation, the emulsion assumes a uniform pink color which is definitely deeper than a comparison system without oil. The alcohol-ether system gave separation and a uniform pink color much darker than the comparison system without the oil. While the cream in the case of ammonium sulfate was white, in some cases there were observed free fat drops. Sodium hydroxide proved the most powerful agent, the cream was deep red, and soon tiny drops of red oil could be noted. These results are easily affected by conditions. Thus heat and stirring with a rod against the side of the tube will liberate free fat from even the white creams. No free fat was ever observed in the ferrocyanic acid tubes but all the rest on longer standing gave gradually increasing amounts. On standing, the blank tubes without added reagents will show free fat, probably due to bacterial attack on the protein. This effect is less with the more finely dispersed emulsions.

DISCUSSION OF TESTS

The picture appears to be that of a precipitation of protein about the oil droplets, and reduced emulsion stability, resulting in clustering and accelerated creaming. In the presence of certain agents these films become permeable to dye, although still keeping oil droplets separate; this effect may be one of dehydration.

It is recognized that the above reagents represent only a small fraction of the possible protein precipitants, capable of affecting such emulsions, and that all these systems constitute far more brutal treatment than could be endured *in vivo*. The whole field of proteolytic enzymes and organisms is untouched. Lehman and Moore[3] reported breaking of the lipemic blood serum from dogs only with ether, and they produced fat embolism in dogs by administration of ether, thus demonstrating a non-traumatic cause. Various other possible mechanisms may be imagined and need to be investigated from this point of view. One of these grows out of the work of Corrau and Lewis,[8] who found that while lecithin stabilizes water-in-oil emulsions and cholesterol promotes the oil-in-water type, the inversion point of systems containing both corresponds approximately to a lecithin-cholesterol ratio of one to one. Since this is the ratio found in human blood serum, the possibility is suggested that high lecithin or low cholesterol content may tend to reverse, and thus to break, the chylomicron emulsion.

In future work on this problem certain factors need to be considered. Fat or oil in the normal chylomicron emulsion cannot be stained with the oil-soluble dye unless and until the protecting protein sheath be removed or made permeable. Neither will the fat in whole milk, and for the same reason. But the microscopic pictures of sections of lungs and brains from cases of fat embolism show capillaries plugged with fat, not with separate protected chylomicrons which do not stain, but with masses of fat many times larger, and stained by the Sudan III. It is true that just as the mechanical rubbing of the emulsion creams did break down the network structure and permit oil to come in contact with dye, so the mechanism of preparing clinical slides may break down aggregates. But it appears improbable that mere aggregation is sufficient, for creaming is reversible and the agitation of the blood stream and the increased venous blood pressure should act to break down aggregates. It does appear that we have to do with relatively massive oil-water interfaces and their properties.

Schade[9] has recently discussed such a point. "Surface tension as well as viscosity, may also disclose death-dealing conditions. If, as a consequence of a break in the vessels, such substances as air or fluid fat, which have high interfacial tension against blood, enter the blood stream, an embolism occurs at the adjoining capillary branches. The heart is not strong enough to bring about in these air or fat droplets a sufficient increase in surface to enable the deformed globule to pass through the small capillaries. The globules tend to remain in the forks of the vessels, blocking the lumen. Should such a blockage occur in the brain or in the lungs at some vital spot, death not infrequently occurs as a result of abnormally large interfacial tension." A very similar picture was given by Pauli[10] who pointed out that such foreign substances in the blood would be surrounded by protein films. "It can readily be shown experimentally that the migration of air bubbles in tubes which are filled with protein solutions meets with unexpectedly great difficulties. In the living organism the danger of the entrance of air bubbles or fat droplets into the circulation is dependent, at least in part, upon similar processes. In both cases we have to do with a solidification of their surfaces which makes the emboli behave in spite of their gaseous or liquid character like solid obstructions to the circulation." If the oil-water interface is important, then added emulsifying agents should reduce this difficulty. Stiffness of protein films might be reduced by such substances as sodium thiocyanate. At any rate, it now appears that the emboli formed are fat globules

[8] CORRAU AND LEWIS, *Biochem. J.*, **18**, 1364 (1924).

[9] SCHADE, H., in ALEXANDER'S "Colloid chemistry," Vol. 2, Chemical Catalog Co., Inc., New York City, **1928**, p. 634.

[10] PAULI, W., "Physical chemistry in the service of medicine," John Wiley & Sons, Inc., New York City, **1907**, p. 130.

which are microscopic and which take the dye. This study of emulsions reveals how difficult it is to effect coalescence of oil droplets in systems far less stable than the chylomicron emulsion.

Dr. Lehman pointed out that the marrow cavity of the human femur has a volume of the order of 0.86 cc. per kilogram of body weight. This figure he compares with his finding that a dog survived injection of 1.5 cc. of cottonseed oil per kg. of dog, and that a dog receiving 1.66 cc. died in eighteen days (3.0 cc. killed within an hour). While there are obvious differences between cottonseed oil in a dog and human fat in a man, these experiments still have weight and, coupled with other considerations advanced above, make it improbable that bone marrow is the sole source of fat emboli. Other experiments reported indicate that obese persons and those with low-melting body fat may be predisposed to fat embolism. In the non-traumatic cases such as etherization, no one could blame the bone marrow as a source. Another possible source of fat is the chylomicron emulsion, and, while there is plenty of fat there available, neither the work of Dr. Lehman nor the present attack reveals a possible mechanism for the coalescence of the chylomicrons. An extension of this work including salt additions and agitation to simulate more closely blood system conditions, is planned.

A third possible source of fat deserves consideration. It seems probable that under emergency conditions some individuals may mobilize from the fat depots of the body this high-energy fuel in such quantities as to exceed even the high dispersive power of the blood proteins. One way to break an emulsion is to add an excess of the dispersed phase. While among physiologists there seems to be some uncertainty concerning the reliability of current methods for measurement of the fat content of the blood, there is a great deal of evidence indicating abnormally high fat content of the blood after trauma, hemorrhage, adrenalin, cyanide, etc.

During the war extensive use was made of injections of solutions of gelatin and of gum acacia in cases of hemorrhage following trauma. The growing use of acacia in connection with major operations may justify greater attention to the problem of the prevention and cure of fat embolism.

The FLAVINS *of* MILK

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HISTORICAL

THE presence of a greenish yellow pigment, now known as lactoflavin, in the aqueous portion of cow's milk was first reported in 1784, which is not many years after the first serious thought had been given to milk production. However, little attention was paid to it until it was reported to be the active vitamin G substance occurring in milk and other dairy products. Upon this discovery in 1933 the energetic vitamin investigators set to work and accumulated such a quantity of experimental data that only now is the true activity of the pigment beginning to unfold itself for accurate classification. The generally accepted name for the flavin substance found in milk is lactoflavin, and it is grouped with the broad class of greenish yellow fluorescent pigments named lyochromes.

Lactoflavin has been isolated from milk by its extraction from powdered whey with various organic solvents and subsequently purified. Pure lactoflavin with the empirical formula $C_{17}H_{20}N_4O_6$ crystallizes as orange-red needles having in aqueous solution a yellow to orange color possessing an intense greenish fluorescence. The pigment in solution is degraded by irradiation with sunlight or ultra-violet light to simpler pigments whose composition is dependent in part on the pH of the solution. In solution it is heat and acid stable but decomposes quite readily on the alkaline side. The synthesis of lactoflavin has apparently been achieved in the compound 6,7-dimethyl-9-isoalloxazine which is reported to have physical, chemical, and vitamin properties identical with those of pure lactoflavin (*5*).

OCCURRENCE AND SOURCE OF LACTOFLAVIN IN MILK

The lactoflavin content of cow's milk varies with breed and ration. Although no exact data are available, an estimate of the quantity found in milk based on average vitamin G potency of milk and of pure lactoflavin would be in the neighborhood of 0.5 to 1.0 p.p.m. According to measurements of color depth in clear whey solutions made from the milk of four breeds, Ayrshire had most pigmentation; Holstein and Shorthorn whey had approximately half the coloration of the Ayrshire; and Jersey whey stood intermediate.

The vitamin G or the lactoflavin eontent of cow's milk apparently is proportional to the amount found in the rations. Furthermore, it has been shown that the amount of greenish yellow pigment in egg whites is distinctly related to the vitamin G in the hen's diet (*10*). Little work, however, has been done in this field.

Vitamin G assays on hays show that alfalfa and clover have more vitamin than timothy and are, themselves, about equal in potency. Hays have higher vitamin G content when cut young than when cut at or after full maturity (*11*), and cows on pasture during the period of

its most vigorous growth produced milk of higher vitamin content than when on mature or over-mature pasture. A significant relation of curing to the vitamin G content of hay was noted by recent workers (*11*). Alfalfa hay, when exposed to dry weather for 96 hours, did not suffer loss of the vitamin; whereas exposure to rainy weather caused a loss of 50% of the vitamin.

NUTRITIONAL AND PHYSIOLOGICAL ACTIVITY OF FLAVIN

The true nutritional activity of flavins in general and lactoflavin as a member of the class may be briefly summed up as follows: lactoflavin is one of the necessary components of the diet because of its growth-promoting properties (*7*); however, lactoflavin alone does not possess all the biological activity formerly ascribed to vitamin G. Recently, competent vitamin investigators have found that pure lactoflavin, or pure flavin, from sources other than milk is not effective in preventing or curing rat or chick pellagra (*3*, *8*, *9*). Furthermore, canine black tongue was produced on a diet which maintained normal growth in rats (*21*), and a dermatitis in chicks was not cured by an addition to their diet of a liver extract rich in the growth-promoting component (*18*). Heretofore it was customary to use the term vitamin G (foreign workers use B_2) interchangeably with lactoflavin; it must now be recognized that, in addition to lactoflavin, there are other heat-stable and water-soluble components responsible for the nutritional activity designated as vitamin G. It is not yet known which component of the vitamin G complex is the preventive factor for certain anemias, cataracts (*2*), and some of the other rarer diseases of vitamin G deficiency.

Milk is adequately supplied with all the components of vitamin G, as evidenced by many nutrition researches, and concentrates of the aqueous portion of milk in the form of powdered whey carry the vitamin without loss. Pure lactoflavin can be isolated from whey powders by extraction with ethanol or methanol and subsequently purified by absorption and elution or by further solvent extraction (*1*, *12*, *19*).

The physiological activity of flavins has manifested itself in connection with biological oxidation-reduction systems; however, its full significance is not very clear. Flavin solutions have the high negative values which characterize the anaerobic potentials of living cells. Warburg and Christian, who prepared a yellow flavin containing ferment, conclude from their studies of its activity that the ferment is an oxygen transferring agent which might act as a respiration enzyme when oxygen is lacking. It has, furthermore, been demonstrated that yeasts of greatest fermenting capacity are those of highest flavin content (*20*). It is apparent that much remains to be learned about the physiological activity of flavin.

LACTOFLAVIN AND RELATED COMPOUNDS

Flavins closely related to or identical with lactoflavin have been found in animal muscular tissues, organs (*17*), blood, and milk; in fowl muscular tissue, organs, and ova; in fish liver to a small extent and in the retina of their eyes to a great extent (*4*, *6*, *13*); in yeasts, mold, and bacteria (*20*); and widespread throughout the green plant world where the molecular ratio, chlorophyll:flavin approximates 2000:1 (*15*). Flavins occur as free pigments and also combined with protein or other colloidal material. In some cases the complex combination possesses enzyme activity. The yellow respiration ferment previously mentioned appears to be such a complex which acts in the presence of phosphoric acid (*16*). The flavin of yeast is reported to be 90% to 100% combined with colloidal material, as compared to the 20% to 25% combination of lactoflavin with protein in milk. The flavin of egg white and yolk known as ovaflavin is believed to be identical with lactoflavin but occurs in a combined form. Lumiflavin results from the degradation of lactoflavin and ovaflavin by irradiation and is of interest in connection with the synthesis of flavins (*14*). It possesses no growth-promoting properties and apparently is biologically inactive.

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A STUDY *of* STUDENT RESULTS *in* QUALITATIVE ANALYSIS

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A study of student results in the qualitative laboratory shows the need for evaluation of each sample analyzed. All ions are not identified with the same ease. Consideration should be given to the fact that certain ions are more likely to be reported when not present than others, and that some ions interfere with the identification of other ions. The results of 18,678 cation and 4073 anion tests are summarized.

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A NUMBER of schemes have been devised by which student results in the qualitative laboratory may be evaluated. Any scheme for the equitable evaluation of student results in qualitative analysis should meet the following requirements. (1) Credit should be given for the separation and identification of ions in ratio to the difficulty of detection of each particular ion. (2) Credit should be given for the ability to establish the fact that certain ions or groups of ions are not present in the sample; or suitable penalties should be assessed for the reporting of the presence of ions which are not in the sample. (3) Consideration should be given the fact that some ions are more difficult to identify when in the presence of certain other ions or when present in small amounts.

This study was made in an effort to obtain a basis for the apportionment of credit in the evaluation of qualitative samples with special reference to requirements 1 and 2.

The source of data for the study was the laboratory records of some 1300 students. These records were kept continuously over a period of seven years, during which time the nature of the work done and the type of samples analyzed were not appreciably changed. The scheme of analysis used was conventional with the exception of the omission of the hydrochloric acid group as indicated by Gelbach.[1] The record of each student was kept in such a manner that it was possible to know the content of each sample, the ions reported correctly, and the ions reported but not present in the sample. The tables following were compiled from those records.

CATIONS

Table 1 indicates the relative difficulty experienced by the students in the separation and identification of each cation. A sufficient number of cases was studied, 18,678 cations being present in the samples studied over the seven-year period. The cation appearing least often in the samples was silver (302 times), and potassium appeared the most often (1710 times). Of the total number of cations present (18,678), 86% (or 16,929) were correctly reported. In the analysis of these samples 2232 cations were incorrectly reported as present. Of these, the ion reported most often was sodium (12% of the 2232 cases) whereas silver was incorrectly reported the fewest times (0.4% of the total). The results of such reports are shown in Table 2.

TABLE 1

PER CENT. OF CATIONS CORRECTLY REPORTED

Cation	*Number of Cases*	*Number of Times Found*	*Per Cent. of Cases Found*
Copper	1193	1134	95
Silver	302	286	95
Nickel	796	746	94
Iron	1029	963	94
Cobalt	749	697	93
Manganese	837	766	91
Lead	1077	983	91
Antimony	508	456	90
Chromium	612	542	89
Bismuth	935	807	86
Sodium	1537	1319	86
Mercury	686	584	85
Potassium	1710	1445	85
Aluminum	779	657	84
Ammonium	906	763	84
Arsenic	430	356	83
Strontium	560	462	83
Cadmium	1078	874	81
Tin	429	340	79
Zinc	938	740	79
Magnesium	1027	805	78
Barium	749	582	78
Calcium	811	622	77

TABLE 2

CATIONS REPORTED BUT NOT PRESENT IN SAMPLES

Cation	*Per Cent. of Total Reported but Not Present*
Silver	0.4
Copper	1.0
Chromium	1.3
Nickel	1.5
Manganese	2.3
Tin	2.6
Mercury	2.8
Cadmium	2.9
Calcium	3.2
Bismuth	3.3
Barium	3.3
Cobalt	3.3
Antimony	3.5
Lead	3.5
Ammonium	4.0
Strontium	4.2
Iron	5.2
Arsenic	6.1
Aluminum	6.3
Zinc	7.4
Magnesium	7.7
Potassium	11.8
Sodium	12.0

It is quite evident from the data in Table 1 that all cations are not detected with the same ease.

[1] GELBACH, "Modified method for cation group I," J. CHEM. EDUC., **10**, 621 (Oct., 1933).

ANIONS

A similar study was made on 4707 anion cases. Of these 4073, or about 86%, were correctly identified. At the same time there were 325 anions reported but not present in the samples. The results are tabulated in Table 3.

TABLE 3

Anion	*Per Cent. of Cases Found*	*Per Cent. of Total Reported but Not Present*
Chloride	95	16
Sulfate	91	17
Iodide	90	1
Carbonate	89	7
Chromate	85	2
Arsenite	83	6
Phosphate	83	9
Sulfite	81	8
Bromide	81	7
Nitrite	80	1
Sulfide	79	1
Nitrate	76	20
Arsenate	70	3
Borate	67	3

CONCLUSION

From the foregoing data it is evident that neither cations nor anions are all identified with the same ease by the student in the laboratory. The application of these data to the evaluation of student results is not nearly as simple as it might seem. Remembering that consideration should be given to the difficulty of identification, the ability to establish the absence of other ions, and the fact that the presence of some ions interferes with the identification of others, it would seem that the most logical scheme would be to evaluate each sample separately. Thus it would be possible to consider the data in Table 1 and to provide suitable reward for the identification of the more difficult ions. In the same manner, suitable penalties might be assessed for failure to find colored ions (when present in reasonable amounts) or for the reporting of ions not present. It is not the purpose of this report to present a scheme for the evaluation of student results but merely to show the need of something better than the pro rata grading system so often used. It will be necessary for the instructor to evaluate the individual samples considering not only the ions present but the quantity of each and the scheme of analysis used. Inasmuch as the scheme of analysis used in this study is that commonly used, and the students not specialized, the data in the accompanying tables might well serve as a guide in sample evaluation in cases in which such data are not available.

ADAPTING *the* PROJECT METHOD *to* UNDERGRADUATE INSTRUCTION *in* CHEMICAL ENGINEERING

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RECENT years have found colleges and universities more receptive than formerly to new theories and technics of teaching. Progressive ideas and experiments in the elementary and secondary schools have gradually seeped into the field of higher education where they have been modified to meet the needs of institutions of various types. The time-honored lecture method—facetiously described as "the process by which information is transferred from the notebook of the professor to the notebook of the student without passing through the head of either"—is being increasingly challenged by newer instructional processes that provide greater opportunity for initiative and purposeful activity on the part of the student.

Among these technics is the so-called project method which has already demonstrated its usefulness in the elementary and secondary fields, and which has more recently been the basis of some educational experimentation among the colleges and universities. This article describes an adaptation of the project technic to a course in chemical plant design given in the senior year of a five-year coöperative program leading to the S.B. degree in chemical engineering. Students enrolled in the course, in addition to the customary academic preparation, also bring with them some understanding of actual industrial requirements based upon their cooperative employment in New England manufacturing plants. Thus the group has both breadth of preparation and a certain maturity of outlook.

The course in chemical plant design is allotted eight clock hours a week throughout both semesters, one hour in class, three hours in the laboratory, and four hours of library work and preparation. Its aim is to teach the student how to attack and carry through to completion a problem involving the design, construction, and operation of a plant for manufacturing some chemical product. Admittedly, this is a large and complicated assignment for an undergraduate to undertake, but ex-

perience over a ten-year period indicates rather definitely that the educational outcome is distinctly worth while.

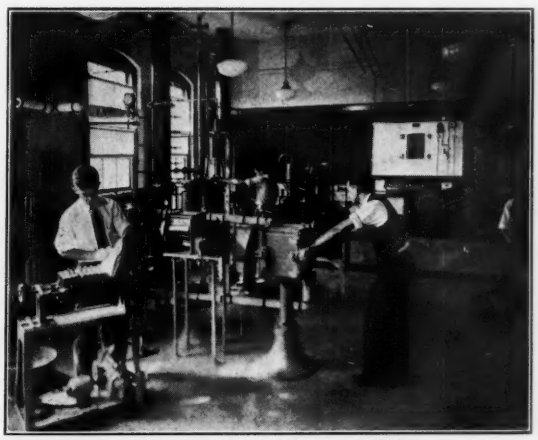
For purposes of instruction the class is divided into squads of three students each. Every squad organizes itself as a firm of consulting chemical engineers whose responsibility it is to prepare a complete report for a group of financiers as to the feasibility of some chemical engineering project. The nature of these projects is determined by the squads themselves after consideration in class of various timely economic needs. Some suggestions are made by the instructor; others are contributed by the students on the basis of their coöperative experience. For example, a student whose cooperative job had been in the tobacco industry in Connecticut noticed that tobacco stems accumulated rapidly and were a waste product. He urged his squad to undertake the design of a plant to retrieve nicotine and potash from tobacco stems, a project of more than academic interest.

Another, at work in the generating plant of a large public utility, observed that the soot which was washed out of smoke from the power plant was merely collected and thrown away. He and his squad are this year trying to find a way to reclaim this waste material and compress it into electrodes or into some slate-like building material. This project will undoubtedly involve problems in the handling of materials, filtration, neutralization, drying, pulverization, separation, the use of binders, and the compression of mass under various temperatures.

SQUAD OF STUDENTS IN CHEMICAL PLANT DESIGN TESTING THE INSULATION VALUE OF THEIR PRODUCT

Some projects are concerned with new products; others with the economical production of highly competitive commodities such as soap powders, facial creams, bleach solutions, and molded resinous products. Either type of project is sound educationally so long as it (1) interests the student, (2) offers him a sufficient number of perplexing problems with which to wrestle, (3) falls within the scope of laboratory facilities, and (4) gives reasonable promise of being economically feasible.

Having selected their projects the squads proceed to survey the literature bearing upon their particular problems. One student seeks to discover the processes already available to manufacture the product, or, if the product is a new one, the processes used in the manufacture of similar products. A second member of the squad studies the present economic situation in the industry concerned, the average capitalization of its units, current trends in the business, etc.; while the third student focuses his attention on quality specifications and markets of the raw materials and finished products with which the project is to deal.

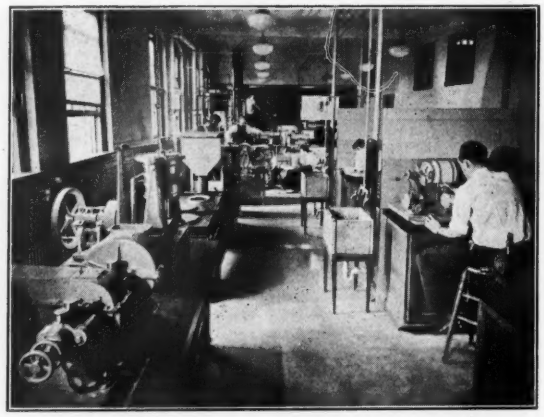


CORNER OF THE CHEMICAL ENGINEERING LABORATORY

Each week in the class hour the students meet to pool their information, discuss problems that have arisen, and make suggestions to each other. The instructor is available as a counselor but avoids lecturing except on occasional controversial issues in which his guidance may be helpful. Early in the course experimentation in the laboratory begins, at first on a test-tube and beaker basis to determine the possibilities of different reactions and later on a semiplant scale. The laboratory is substantially equipped with a large variety of apparatus for experimentation in the unit processes of chemical engineering. When apparatus not already in the laboratory is needed the students are encouraged to build small working models themselves in order that they may encounter some of the difficulties that arise in the design of chemical plant equipment and learn how to overcome them.

After trying out various processes experimentally each squad proceeds to select equipment for the plant it is designing. In this connection a sizable file of manufacturer's bulletins containing specifications of various machines and cost data is maintained by the instructor for class reference. When information needed on a project is not found in this library, the students write directly to the manufacturer. Such data are filed for the use of future classes.

After the equipment has been selected, the machines are located and flow sheets are prepared showing the routing of the materials through the plant. Frequently students find it helpful to make visits of inspection to various plants in the vicinity in order to get first-hand information about some aspect of their project. In this respect manufacturers have been most coöperative, often giving more freely than requested of their time and facilities.



VIEW IN THE LABORATORY SHOWING SOME OF THE EQUIPMENT AVAILABLE FOR SEMIPLANT SCALE OPERATION

During the latter part of the course the weekly hour in class is given over to special reports by individual students on topics of general interest to all squads. Factors such as plant location, patents and copyrights, marketing, safety engineering, transportation, etc., are typical of those presented in outline form and then discussed by the entire group. Students acquire more useful information and enter into the discussions with greater zest on this plan than they formerly did when the instructor gave a series of lectures on the same issues.

The final report on each project is written jointly by the members of each squad, responsibility for specific sections being assigned to an individual by arrangement with the instructor. In this way a measure of the individual achievement of each student is obtained. Further check-up is secured by means of a specially designed notebook in which each student records his class notes, results of library research, observations on visits to industrial plants, and laboratory data. The notebook is provided with carbon sheets so that two copies of all entries are made, one for the student and one for the instructor. Thus the course involves both the ability to coöperate with fellow workers and the ability to do technical research. The final report submitted by each squad includes a statement as to the division of responsibilities among the group, a review of the literature bearing on the project, an account of experimental work and the conclusions drawn therefrom, a discussion of plant location, the layout of equipment with description of each piece, and flow sheets, the cost of equipment ready to operate, yearly labor costs, including administrative salaries, an estimated operating statement for one year, and general summary with recommendations.

It may be argued that such a report is beyond the capacity of any group of undergraduates to prepare in adequate fashion in the course of a single year. How can they possibly get a sufficient grasp of the many and varied factors involved in such an undertaking, correlate them all, and weave their findings into a completely reliable report?

As a matter of fact, most of the reports worked out by students in the course are surprisingly detailed. There is no question but that the students take pride in turning in the best piece of work of which they are capable. But even if the job isn't one hundred per cent. perfect the student has had a stimulating educational experience. He has learned a great many facts incidentally, even though he has undoubtedly overlooked other facts of equal importance. But the important consideration is that he has matched his abilities against a real live project in which the procedure was not all mapped out for him in advance. Before he could begin work he had to decide what his problems were, how they should be attacked, and in what order. It is this stimulus to the student's initiative, this appeal to his natural desire to direct a responsible piece of work, and the awakening in him of the realization that he must chart his own course that contribute most to his educational development.

Writing on the learner and his attitude, G. C. Myers records the following passage indicative of a serious lack in much college teaching:[1]

> "I remember that while in college I was able there to pass respectably and do the experiments with acceptable technic, but I often was embarrassed if some classmate asked me how to proceed in this experiment or that, unless I had my notes to help me. It is easy to do the average laboratory course with excellence without having mastered what appears to have been mastered. If, on the other hand, every experiment I performed I had felt as a real problem, or as a part of a problem I was soon to be confronted with, or of one I had met without having recognized or, if recognized, had failed to solve till then, I would have mastered such experiments for life."

Against the first-mentioned kind of learning on the part of our students we need continually to guard. The technic outlined in this paper aims at substituting for stereotyped instruction an approach based upon a large measure of student participation and calculated to develop habits and points of view that will be permanently useful. Unfortunately, there is no objective measure of the success of this course in accomplishing its purposes. The only criteria available are the comments of students and the observations of instructors as to the relative worth of this method compared with the lecture-laboratory plan formerly followed. If these criteria are significant the project method is markedly superior.

[1] MYERS, G. C., "The learner and his attitude," Benjamin H. Sanborn and Company, Chicago, pp. 188–90.

SOME DEPARTURES *from* CLASSICAL LABORATORY METHODS *in* GENERAL CHEMISTRY

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DURING the past seven years the author has been using a laboratory manual which embodies some appreciable departures from that which may be called the classical manual for general college chemistry. This manual, which has been worked out by the author and her colleagues, attempts to make the laboratory period of general chemistry a more valuable study period than it has proved frequently to be in the past. Since an appreciable amount has been accomplished during the years that the newer methods of this manual have been employed, and since the whole subject of the laboratory work of general chemistry appears to be again under fire as witnessed by the symposium at the spring, 1935, meeting of the American Chemical Society and the articles which have been appearing in the JOURNAL OF CHEMICAL EDUCATION* within the past few months, it seems to the author that the readers of this journal may be interested in the work along this line being done at Hollins College.

The two and a fraction representative experiments given below, together with the questions on the report sheets for these experiments, will suffice to give the reader some ideas of the aims and methods of the abovementioned manual. In the experiments given below the reader will note, among other things, that the student reports on experiments in the form of answers to specific questions on each experiment, that the questions require the use of information gained from lecture experiments and previous laboratory exercises, and that the student plans some of his own work. During the course of the year the students plan an appreciable amount of their experimental work. This, however, may involve only slight modifications of directions, but the freshman is inexperienced and finds even modifications none too easy. Neither does he find any too easy the answering of direct questions regarding his experimental work. Even very simple questions which must be answered directly with complete, terse sentences seem more difficult and demand better knowledge of the subject than a description of operations which the students can produce in fairly good form without a clear understanding of the material.

The paragraphs below contain the directions and questions on report sheets for representative experiments selected from the section of the laboratory manual covering work on equilibrium.

Experiment 29.—A study of several chemical reactions to determine whether they are reversible. There are three simple methods of testing for the slight reversibility of metathesis reactions in solution in which a precipitate is formed.

(1) The addition of an excess of one of the products of the reaction (Law of Mass Action) in an effort to reverse the reaction to an appreciable extent—especially applicable when one of the products is an acid. (Recall lecture experiment.)

(2) The removal of one of the products of the reaction or of one set of ions from the filtrate—especially applicable when one of the products of the reaction is an acid or a base. (Recall lecture experiment.)

(3) The testing for the presence of one set of ions of the "insoluble" compound in the filtrate by the addition to the filtrate of some reagent which will form with the ions whose presence is being tested a compound that is less soluble than the first precipitate—especially applicable in the case of two salts.

(*a*) To 10 ml. of calcium chloride solution slowly add dilute sulfuric acid solution until you think that precipitation is complete. Filter the mixture and test the filtrate for complete precipitation by adding to the filtrate a drop or two more of sulfuric acid. If no precipitate is formed at this point the precipitation may be considered to be as complete as is obtainable with the reagents being used. Wash the precipitate several times by blowing a spray of water over it from your wash bottle and allowing the water to drain well between washings. Write an equation for the reaction which has taken place. What is the precipitate? What acid has been formed and is present in the filtrate? Test the reversibility of this apparently complete reaction by the first method given above. To do this transfer a small amount of thoroughly washed precipitate to a test-tube containing about a milliliter (or less) of water and mix the two. Then add 3–5 ml. of a concentrated solution of the proper acid (what?) to test the reverse of the reaction just carried out and shake the mixture vigorously and persistently for several minutes, if necessary, in order to decide whether the precipitate will dissolve, or react with the acid. If the precipitate dissolves the reaction between the calcium chloride and the sulfuric acid was undoubtedly somewhat reversible (why?), although, for ordinary practical purposes, it may be considered complete.

(*b*) To 10 ml. of calcium chloride solution slowly add a solution of sodium sulfate until precipitation is as complete as is obtainable. (How tested?) Add 3–4 drops excess of sulfate solution after you are sure that precipitation is complete. (Why?) What does the filtrate contain if the reaction is absolutely complete? What does it contain if the reaction is somewhat reversible? Test the reversibility of this reaction by the third method given above. To do this, test the filtrate for the presence of calcium ions by adding to it a solution of some salt which will form with the calcium ions (if present) a compound less soluble than the calcium sulfate. (See table of solubilities in appendix.) The formation of a precipitate on addition of the reagent selected shows the presence of some free calcium ions in the filtrate and

* *Cf.* "An experiment on chemical equilibrium for beginners," L. P. EBLIN, J. CHEM. EDUC., **12**, 324–5 (July, 1935); "The contribution of laboratory work to general education," H. I. SCHLESINGER, *ibid.*, **12**, 524–8 (Nov., 1935); and others.

thus proves that the first reaction was somewhat reversible. (How?) Why would not testing for the presence of sulfate ions in the filtrate do as well in this case as testing for the calcium ions? How could you have modified your procedure to have made a test for the sulfate ions a proper test for the reversibility of the reaction?

(*c*) To 10 ml. of silver nitrate solution slowly add a solution of sodium sulfate until precipitation is complete (how determined?) and then add 3–4 drops excess of the sulfate solution. Test the reversibility of this reaction by the third method given above. For which ions of the precipitate, the silver or the sulfate ions, should the filtrate be tested? (Why?) How could you modify the procedure of this experiment to test the filtrate for the ions of the precipitate for which you are not testing here?

(*d*) Write an equation for each of the reactions indicated below and decide which one of them would be most nearly complete when carried out in solution. Be sure you know the basis upon which you make your prediction:

1—Barium nitrate plus potassium chromate
2—Silver nitrate plus potassium chromate
3—Lead nitrate plus potassium chromate

(*e*) Carry out a reaction of your own selection in which an "insoluble" compound (salt, base, or acid) is formed, and test the reaction for slight reversibility by one of the above methods. Report to an instructor the materials to be used and your method of procedure before starting your experiment. Include in the proper place on your report sheet a clear, brief report of the results of this experiment.

The questions on the report sheets for Experiment 29 are given below, but the blank spaces left for the answers are omitted. The student is expected to answer each question in the form of clear, complete, terse sentences, except where tabulation in phrases is indicated. The student may, in many cases, use tabulations following an explanatory sentence, but a student's grade is lowered for failure to make the answer complete and clear, independent of the presence of the question. The reasons for this, particularly in view of the present-day overemphasis on completion tests and true-false tests in secondary schools, are too obvious to need comment. A space which is considered adequate for an answer directly to the point is to be found immediately following the question to be answered. The size of the space, which is quite sufficient for the better students, serves to curb the verbose student and help him learn to write briefly and to the point. The questions for Experiment 29 are as follows.

(1) Express with an equation the reaction between calcium chloride and sulfuric acid.

(2) If you had stopped your work after carrying out the above reaction what would have been your conclusion in regard to the reversibility of the reaction? Why?

(3) Tell briefly how you tested the possible reversibility of the reaction in #1, give the results of the test, and tell why it was a convincing one. Of what principle did you take advantage in making this test?

(4) Express with an equation the reaction between calcium chloride and sodium sulfate. Does the reaction appear to be complete or reversible? Give the reason for your answer.

(5) Mention each of the components present in the filtrate from the reaction represented in #4, (*a*) if the reaction is complete, (*b*) if the reaction is incomplete, or slightly reversible. In the latter case tell which ions will be present in the smallest quantity as the experiment was carried out.

Components if reaction is complete	Components if reaction is incomplete

(6) Tell how you tested for the ions given in the second list above as the ones present in the smallest quantity. Give the basis upon which you selected the reagent used in making the test, and give the results of your test.

(7) Give your conclusion in regard to the reversibility of the reaction in #4 telling why the test applied in #6 was convincing.

(8) Why would not testing for the sulfate ions in the filtrate do as well in the above case as testing for calcium ions?

(9) How could you have modified your procedure to make a test for the sulfate ions a proper one for the reversibility of the reaction?

(10) Express with an ionic equation the reaction between silver nitrate and sodium sulfate.

(11) If the reaction in #10 is reversible to any extent what ions will be present in the filtrate in smallest quantity as the experiment was carried out? Why? If the above reaction is absolutely complete what ions will not be present in the filtrate?

(12) Briefly give the test applied to the reaction in #10 to determine its possible reversibility. Give the results and your conclusions and tell why the test made was a convincing one.

(13) How could you modify this experiment (in #10) in order to make a test for sulfate ions in the filtrate a proper test for reversibility?

(14) Give the equations for the reactions considered in part (*d*) and state, together with the basis upon which you make your conclusion, which of the three reactions would be most nearly complete and which one would be most reversible.

(15) Give a brief report on the experiment that you planned and carried out in part (*e*).

(16) In a few sentences tell how the second method, as given in this experiment, of testing for slight reversibility of seemingly complete metathesis reactions in dilute solution was demonstrated in a lecture experiment.

The directions for Experiment 30 and the questions on the report sheets for this experiment are as follows.

Experiment 30.—A study of the loss of material through incomplete precipitation. As observed in Experiment 29, metathesis reactions apparently complete in solution due to formation of precipitates are really slightly reversible because the compound composing the precipitate is not *absolutely insoluble*. The fact that a compound is not completely insoluble results in the loss of a trace, or more, of the compound or some one of its ions during precipitation from water solution. Frequently a chemist is interested in removing just certain positive or negative ions from a solution. It is, therefore, important in attempting to remove a set of ions from a solution as completely as possible to select a reagent which will combine with the ions in question to form with them the least soluble salt possible and to use the precipitant in relatively large excess when such excess does not interfere with subsequent reactions.

(*a*) To 15 ml. of barium chloride solution add enough of a solution of a suitable salt to precipitate the barium ions as barium carbonate. (In carrying out this and other precipitations note the concentration of the solutions as given on the bottles and add slightly more than the correct volume of the required reagent to react completely with the chemical in question.) What volume of precipitant, in this case, should be used if its concentration is equivalent to that of the barium chloride solution? What volume, if its concentration is half that of the barium chloride solution, etc.? Filter the above mixture and measure the volume of the filtrate with the graduated cylinder. (What about the accuracy of this measurement?) On the assumption that the filtrate is a saturated solution—extremely dilute though it may be—of barium carbonate, calculate the weight in grams of the barium carbonate lost in the filtrate. (See table of solubilities in appendix.) What weight of barium ion is lost in the filtrate? What source of inexactitude are you permitting in your calculations at this point? How does one know that the filtrate is a saturated solution of barium carbonate?

Prove the presence of the slight trace of barium ions (and thus the slight reversibility of the reaction) in the filtrate by add-

ing a suitable reagent. (What? How selected? See Experiment 29.) Do you find your theory in regard to the loss of some barium ions in the above filtrate correct?

What reagent should have been added to the barium chloride in the first place to have precipitated the barium ions most completely, or to have resulted in the loss of the minimum amount of barium ion during the precipitation and filtration? What weight of barium ion would have been lost in the above filtrate if this reagent had been used instead of the carbonate? (In making the calculations, assume that the same volume of filtrate would have been formed in both cases.) Is the amount lost in either case a weighable quantity?

(*b*) Write equations showing what reagent to add to each of the following compounds to precipitate most completely (according to table of solubilities in appendix) the ions indicated in each case. In each of the instances give the weight in grams of the precipitate which would be lost in 150 ml. of filtrate. Is it a weighable quantity in any case?

1—Lead ions from a solution of a lead salt
2—Silver ions from a solution of a silver salt
3—Zinc ions from a solution of a zinc salt
4—Calcium ions from a solution of a calcium salt
5—Lithium ions from a solution of a lithium salt

Which of the above reactions would be most nearly complete, or least reversible? Why? Which of the three positive ions used with potassium chromate in Experiment 29(*d*) would remove the chromate ions most completely from a solution? Why?

The questions on the report sheets for Experiment 30 are as follows.

(1) Express with an ionic equation the precipitation of barium carbonate in this experiment.
(2) Tell briefly how the possible reversibility of the above reaction was tested and give the results of the test.
(3) Give the volume of the filtrate obtained by filtering the mixture in #1 and also give the calculated amount of barium carbonate lost in the filtrate. (Make calculations here.)
(4) What weight of barium ion was lost in the barium carbonate in the filtrate? (Make calculations here.) What slight inaccuracy do you permit in making this calculation?
(5) On the assumption that the volume of filtrate would have been the same if the barium ions had been precipitated as completely as possible instead of being precipitated as carbonate, calculate the barium compound which would have been lost in that case. (Give the calculations here.) Compare the weight of barium ion lost in this compound with that lost in the barium carbonate.
(6) Write equations showing what reagent to add to solutions of a salt of each of the following metals in order to precipitate most completely the ions indicated in each case. (Select any soluble salt of the metal in writing your equations.) Also give the weight of precipitate which would be lost in 150 ml. of a solution in each case. Is it a weighable quantity?

1—Lead ions
2—Zinc ions
3—Silver ions
4—Calcium ions
5—Lithium ions

(7) Which of the reactions in #5 would be most complete, or least reversible? Why?
(8) Which of the three positive ions used with potassium chromate in experiment 29(*d*) would remove the chromate ions most completely from a chromate solution? Why?

As a third sample of the experiments in the laboratory manual being considered the following extract from an experiment on hydrolysis is given:

Experiment 36.—A Study of Hydrolysis.....
(*f*) Prepare by a metathesis reaction in solution small quantities of silver oxide (why not hydroxide?) and silver borate, respectively, by adding solutions of the same chemical to a solution of silver nitrate. (Recall a lecture experiment in selecting concentration of solutions.) Carefully explain to yourself how the same reagent can be used with the silver nitrate to prepare two different compounds of silver.

(*g*) Add a small, transparent crystal of antimony trichloride to about ten milliliters of distilled water and note the change in appearance of the surface of the crystal after a moment or two. Keeping in mind the nature of the hydroxide and the acid from which the antimony chloride is derived, interpret the results noted. Shake the mixture vigorously and explain why the antimony chloride seems not to dissolve. (Is antimony chloride listed as an insoluble compound?) What is the finely divided insoluble material? Write an equation expressing its formation. Applying the principle of Le Chatelier, select the best reagent to dissolve the precipitate (Experiment 32) or to shift the equilibrium back to the formation of antimony chloride. Try the effect of the reagent selected. Add enough of it to "dissolve" the precipitate. (Use concentrated solution. Why?) Write an equation expressing the dissolving. What is the antimony compound present at this point?

Add a few drops of the clear solution just formed to 300–400 ml. of distilled water and stir vigorously and persistently; note the results. Interpret the results and write an equation expressing the change. Which of the reagents in the reaction which first took place above in (*g*) has been greatly increased here by the addition of the 300–400 ml. of water? Does the "stress" applied in the form of an increase of this compound produce the shift in equilibrium which you would predict in accordance with the principle of Le Chatelier? Was the method of shifting the equilibrium to the formation of the precipitate the second time the same as, or different from, that used in dissolving the precipitate?

The questions from the report sheets of Experiment 36 which cover parts (*f*) and (*g*) follow.

(10) Tell briefly how you prepared silver oxide and silver borate from solutions of the same compounds. Explain clearly how the same reagents gave different results.
(11) In what former case did you find the concentration of a reagent very important to the success of a reaction? (Experiment 31.)
(12) Give and interpret the results noted on adding antimony chloride to water. Express the results with an equation.
(13) Give an equation showing how you dissolved the insoluble compound formed in #12.
(14) Give an equation showing the results of adding some of the compound formed in #13 to a relatively large volume of water. Compare with the results in #12.
(15) What type of "stress" or "stresses" have you used in shifting the equilibrium first in the direction indicated in #12, then in the direction indicated in #13, and again in the direction given in #14?
(16) In making a solution of antimony chloride what reagent, as indicated by the results of this experiment, must be added to the mixture to "hold" the antimony chloride in solution?
(17) Bismuth nitrate shows a behavior similar to that of antimony chloride. Suggest a reagent to "hold" bismuth nitrate in solution. Of what principle did you take advantage in selecting the reagent?

It is hoped that the above examples of experiments from the laboratory manual here discussed have served to illustrate the method which the author has been using for some years with more success than she was ever able to obtain with the older methods. It is believed that the above experiments will indicate fairly clearly the value of direct questions, and the advantages of this form of report over the older method of "writing up" experiments. The author believes, however, that emphasis should be put upon the fact that there are

distinct and separate report sheets for each experiment. She would be the last to advocate a form sheet which could be used alike for all experiments, or a report that bordered on completion tests in which the underlining or circling of words, or the use of phrases would constitute a report on a laboratory experiment. While the author would not claim that the above experiments and questions guarantee accurate experimental work on the part of the student, careful observation, correct conclusions, and as complete a correlation of the student's knowledge as is desirable, she is willing to claim on the basis of seven years' observation that they, and the other experiments in the manual, have helped toward these ends, that the student can do little hedging and beating about the bush in this type of report, and that he cannot occlude his haziness in a mass of relevant and irrelevant descriptive material. The manual has contributed toward making the laboratory period a pleasanter and more profitable study period, and much has been accomplished in the way of helping the students learn to think and to reason in terms of the great principles of chemistry. Also, through the course discussed (which, by the way, deviates considerably from the order of presentation of material in available texts) the students are becoming more and more conscious of the scientific method and of science as a "way of work," or a "method of procedure," and the course in general chemistry is making, more nearly than in the past, the invaluable contribution to a general, cultural education that it should and can make.

The ESTIMATION *of* BOILING POINTS *as an* AID *in* ORGANIC RESEARCH

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The boiling point is the most important physical constant of a liquid. The boiling point at 760 mm. can be closely estimated from data obtained at a reduced pressure if certain precautions are observed to insure the accuracy of the experimental determination. Methods have been developed which make possible the approximate calculation of the boiling point at standard pressure of unknown compounds to within a few degrees or less. The wider use of these methods would eliminate many of the incorrect boiling-point data which are at present accumulating in the literature. Examples are cited of the application of these principles in detecting erroneous data. Erroneous values in the literature for the boiling points of 1-chloropentane, 2-chloropentane, 3-chloropentane, 1,3-dichloro-2-methylpropane, 1,3-dichloropropane, 1,4-dichlorobutane, 2-methyl-1-nitropropane, and 1-pentene are corrected, in several cases, for the first time.

✦ ✦ ✦ ✦ ✦ ✦

INTRODUCTION

IN THE routine characterization of an organic liquid it is customary to give its boiling point, density, refractive index, and also the melting point if it is not inconveniently low. An examination of the literature shows that in the case of incompletely characterized liquids the boiling point is stated more often than any of the other constants. This is probably because the boiling point is obtainable from the data recorded in the routine purification of the compound by distillation and does not involve any extra effort. The inherent value of the boiling point in the identification of a liquid is thus enhanced by the fact that it is more often available than any other constant, by the wide range of boiling points exhibited by organic compounds, and, finally, by the fact that there is a great deal of regularity in the boiling points of related compounds.

This last fact is in marked contradistinction to the situation with respect to melting points—which at present are usually unpredictable—and often enables the worker to obtain from the boiling point at least a strong indication concerning the relative probabilities of two or more possible structures for a new compound.

METHOD OF CORRECTING BOILING POINTS TO STANDARD PRESSURE

Some of the fundamental principles of vacuum distillation have been pointed out by K. C. D. Hickman (*1*). Grave errors are often made in the determination of boiling points in ordinary vacuum distillation because of superheating, the lowering of the partial pressure of the substance being distilled by the current of air usually used to prevent bumping, and, particularly at pressures below 10 mm., by the very appreciable pressure drop occasioned by the rapid flow of large quantities of vapor through apparatus of ordinary dimensions. It is easy to forget that there is 760 times as great a volume at 1 mm. as at 760 mm. Many boiling points in the literature which have been obtained at low pressures are therefore not particularly dependable, but if (1) the

usual capillary is replaced by a layer of crushed, screened pyrex sintered to the bottom of the distilling flask, (2) an adiabatic rectifying column is used so that superheating is avoided, and (3) the apparatus is suitably designed to give accurate and constant pressure readings, correct values can easily be obtained.

These boiling points may be converted to values at 760 mm. by a number of different procedures. Probably the most convenient one is the graphical method devised by Germann and Knight (*2*). Their graph can be used, however, only between 500-mm. and 900-mm. pressure, and "vacuum" distillations are usually carried out at pressures below this range.

The method of Craghoe (*3*) has been somewhat simplified by Newton and the writer (*4*). The correction of the boiling point to the value obtainable at atmospheric pressure may be made by using the equation:

$$(1)\ \Delta t = \frac{(273.1 + t)\ (2.8808 - \log p)}{\phi + 0.15\ (2.8808 - \log p)} \qquad (1)$$

where Δt = degrees C. to be added to the observed boiling point,
t = the observed boiling point,
$\log p$ = the logarithm of the observed pressure in millimeters of mercury,
ϕ = the entropy of vaporization at 760 mm.

The value of ϕ may be estimated from the graph and Table 1. Substances not included in the table may be classified by grouping them with compounds which bear a close physical or structural resemblance to them.

TABLE 1

Compound	*Group*	*Compound*	*Group*
Acetaldehyde	3	Halogen derivatives	Same group as though halogen were hydrogen
Acetic acid	4		
Acetic anhydride	6		
Acetone	3		
Acetophenone	4		
Amines	3	Heptylic acid	7
n-Amyl alcohol	8	Hydrocarbons	2
Anthracene	1	Hydrogen cyanide	3
Anthraquinone	1	Isoamyl alcohol	7
Benzaldehyde	2	Isobutyl alcohol	8
Benzoic acid	5	Isobutyric acid	6
Benzonitrile	2	Isocaproic acid	7
Benzophenone	2	Methane	1
Benzyl alcohol	5	Methanol	7
Butylethylene	1	Methylamine	5
Butyric acid	7	Methyl benzoate	3
Camphor	2	Methyl ether	3
Carbon monoxide	1	Methyl ethyl ether	3
Carbon oxysulfide	2	Methyl ethyl ketone	2
Carbon suboxide	2	Methyl fluoride	3
Carbon sulfoselenide	2	Methyl formate	4
m- and *p*-Chloroanilines	3	Methyl salicylate	2
		Methylsilicane	1
Chlorinated derivatives	Same group as though Cl were H	1- and 2-Naphthols	3
		Nitrobenzene	3
		Nitromethane	3
o-, *m*-, and *p*-Cresols	4	*o*-, *m*-, and *p*-Nitrotoluenes	2
Cyanogen	4		
Cyanogen chloride	3	*o*-, *m*-, and *p*-Nitrotoluidines	2
Dibenzyl ketone	2		
Dimethylamine	4	Phenanthrene	1
Dimethyl oxalate	4	Phenol	5
Dimethylsilicane	2	Phosgene	2
Esters	3	Phthalic anhydride	2
Ethanol	8	Propionic acid	5
Ethers	2	*n*-Propyl alcohol	8
Ethylamine	4	Quinoline	2
Ethylene glycol	7	Sulfides	2
Ethylene oxide	3	Tetranitromethane	3
Formic acid	3	Trichloroethylene	1
Glycol diacetate	4	Valeric acid	7
		Water	6

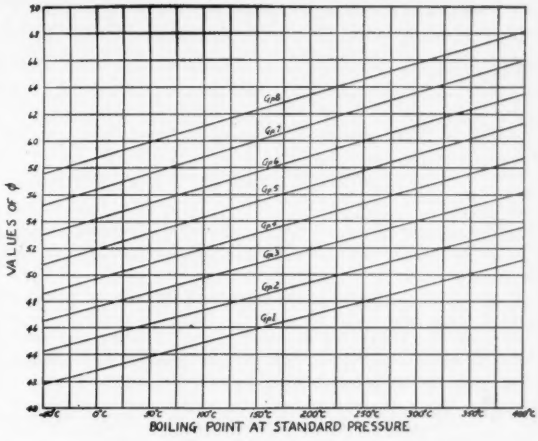
Example 1. Benzene boils at 20°C. at 75 mm. pressure. What is the normal boiling point? We do not find benzene in the table but we find hydrocarbons in group 2, and a group 2 compound with a boiling point of 20° has a ϕ of 4.6.

Substituting in the equation:

$$\Delta t = \frac{(273.1 + 20)\ (2.8808 - 1.8751)}{(4.60 + 0.15)\ (2.8808 - 1.8751)} = 62°$$

Adding this to 20° gives 82° as a first approximation.

The graph shows that the ϕ for a compound of group 2 boiling at 82° is 4.72 instead of 4.60 which we originally used. Since ϕ is in the denominator, this increase will lower our Δt by the ratio, 4.60/4.72, or the corrected Δt is $62 \times (4.60/4.72) = 60.4$. Adding Δt to t gives 80.4° as a second approximation.



The formula can best be used in a slightly different form when the reverse calculation is desired, *i. e.*, when one calculates the vapor pressure at a given temperature lower than the normal boiling point.

$$(2)\ 2.8808 - \log p = \frac{\phi\,\Delta t}{273.1 + t - 0.15\,\Delta t}$$

Example 2. Alcohol boils at 78.4°C. What is its vapor pressure at 20°C.?

Substituting in equation (2):

$$2.8808 - \log p = \frac{6.06 \times 58.4}{293.1 - (15 \times 58.4)} = 1.245$$

$$\log p = 2.8808 - 1.245 = 1.6358$$

$$p = 43.2 \text{ mm.}$$

Here no second approximation is necessary since the correct value of ϕ was taken immediately, the normal boiling point having been known.

ESTIMATION OF BOILING POINT AT 760 MM. FROM FORMULA

The estimation of boiling points at standard pressure from the formula of the compound enables the chemist to compare these values with the ones obtained experimentally at 760 mm. or with those found at diminished pressure and corrected to 760 mm. In case of a serious discrepancy the possibility of an erroneous identification of the compound or of an inaccurate boiling-point determination may properly be considered.

A. *Method of Calculation from a Single Homolog*

This has been explained by Kamm (*5*). An example will suffice to indicate the general procedure.

Problem 1. Assuming that the replacement of a hydrogen atom by a methyl group at the end of the chain raises the boiling point 20°, that a similar replacement by an alpha methyl group (*i. e.*, a methyl group substituted on a carbon atom already holding an OH) raises it 2°, and that methyl groups in intermediate positions have proportional effects, calculate the boiling points of the eight isomeric amyl alcohols from the boiling point of *n*-propyl alcohol (97.8°C.).

Solution:

		Estimated b. p., °C.	*Correct b. p., °C.*	*Error, °C.*
1-pentanol	$97.8 + 20 + 20 =$	137.8	138.00	−0.20
2-pentanol	$97.8 + 20 + 2 =$	119.8	119.28	+0.52
3-pentanol	$97.8 + 20 + 2 =$	119.8	115.40	+4.40
2-methyl-1-butanol	$97.8 + \frac{(20 + 2)}{2} + 20 =$	128.8	128.0	+0.8
3-methyl-1-butanol	$97.8 + 20 + 2/3(20 - 2) + 2 =$	131.8	132.00	−0.2
2-methyl-3-butanol	$97.8 + 2 + \frac{(20 + 2)}{2} =$	110.8	111.6	−0.8
2-methyl-2-butanol	$97.8 + 2 + 2 =$	101.8	101.8	0.0
2,2-dimethyl-1-propanol	$97.8 + 2\frac{(20 + 2)}{2} =$	119.8	114.0	+5.8

While most of the above agreements are exceedingly close, the values for 3-pentanol and 2,2-dimethyl-1-propanol leave room for improvement.

If the method is extended to the glycols it fails completely, as the following data show:

Problem 2. Using the above method calculate the boiling points of the glycols obtainable by adding alpha methyl groups to ethylene glycol whose boiling point is 197.5°C.

		Estimated b. p., °C.	*Correct b. p., °C.*	*Error, °C.*
Propylene glycol	$197.5 + 2 =$	199.5	189	+10.5
Isobutylene glycol	$197.5 + 2 + 2 =$	201.5	177	+24.5
Butane-2,3-diol	$197.5 + 2 + 2 =$	201.5	184	+17.5
Trimethylethylene glycol	$197.5 + 2 + 2 + 2 =$	203.5	177	+26.5
Pinacol	$197.5 + 2 + 2 + 2 + 2 =$	205.5	172.8	+32.7

While a decrease in boiling point upon ascending an homologous series is admittedly exceptional, an error of more than thirty degrees indicates that a better method is at least possible. The following procedure for calculating boiling points has been used in this laboratory with good results for several years and has always given calculated boiling points which are very close to the correct experimental values.

B. *Calculation from Most Closely Related Compounds*

(1) Find the known compound most similar to the new compound whose boiling point is to be estimated.

(2) Find the increment of molecular formula or structure by which the known compound differs from the new compound.

(3) Find the effect of this increment upon the boiling points of closely related compounds.

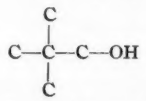
(4) Add or subtract the value of (3) to or from the value of (1).

It should be remembered also that a given increment usually has less effect upon the boiling point of a high-boiling compound than upon that of a low-boiling compound, but that the first member of a given homologous series often has an exceptional boiling point.

The method is best understood by examples and for this purpose we have selected ones in which errors in the literature have been made evident by this type of calculation. As a preliminary, however, let us clear up some of the errors in the calculated results of Problems 1 and 2.

The worst error (5.8°) in the solutions of Problem 1 was in estimating the boiling point of 2,2-dimethyl-1-propanol. This alcohol differs from 1-propanol by the increment of two CH_3 groups in place of hydrogen atoms on the central carbon atom. This is the same increment as between 1-propanol and isobutyl alcohol.

1-propanol, b. p. 97.8 2-methyl-1-propanol, b. p. 107.3°

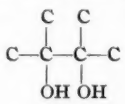


2,2-dimethyl-1-propanol

The solution by the method of most closely related compounds therefore is: $97.8 + 2(107.3 - 97.8) = 116.8$°C. and the error is 2.8°C. instead of 5.6°C.

The worst error (32.7°C.) in the solution of Problem 2 was the value for pinacol. This glycol differs from trimethylethylene glycol in the same way that the latter differs from 2,3-butanediol, namely, by the addition of a methyl group which converts a secondary OH to a tertiary OH.

2,3-Butanediol, b. p. 184° Trimethylethylene glycol, b. p. 177°



Pinacol

The solution by our method therefore is $177 - (184 - 177) = 170$° which is in error by 2.8° instead of 32.7°.

Problem 3. The boiling points of 1-, 2-, and 3-chloropentane given in the *International Critical Tables* are, respectively, 105.7°, 105°, and 105°. Only one of these is approximately right. Find which one it is and correct the other two values.

Solution: The following boiling points for the normal alkyl chlorides are accurately known: ethyl chloride 12.2°, *n*-propyl chloride 46.60°, *n*-butyl chloride 78.50°. The boiling-point increments for each successive CH_2 group are therefore 34.4° (ethyl to propyl) and 31.9 (propyl to butyl). The probable value for the next increment (butyl to amyl) is therefore about 30°. The value for butyl chloride, 78.50° + 30° = 108.5° for 1-chloropentane.

Recently this value has been very carefully determined experimentally as 108.35° (7).

The following dependable values are also to be found: 2-chloropropane 34.8° and 2-chlorobutane 68.25°. The average differences between the primary and secondary isomers is therefore obtainable as follows: 46.60 − 34.8 = 11.8°, 78.50 − 68.25 = 10.25, $\frac{11.8 + 10.25}{2} = 11.0$°. The correct value for 2-chloropentane may now be estimated: 108.35 − 11.0 = 97.35°.

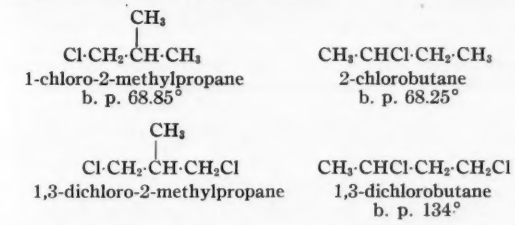
The boiling point of 3-chloropentane should be the same since it contains the same structural groups: two CH_3—, two —CH_2—, and a —CHCl— all arranged in a straight chain.

	Correct Values	Critical Tables Values	Error	Estimated Values	Error
1-chloropentane	108.35°	105.7°	−2.65°	108.5°	+0.15°
2-chloropentane	96.7°	105°	+8.3°	97.25°	−0.55°
3-chloropentane	97.3°	105°	+7.7°	97.25°	−0.05°

The "correct values" have been either obtained or checked in this laboratory.

Problem 4. The compound 1,3-dichloro-2-methylpropane has been reported as boiling at 45°/10 mm. (*6*). Show that this is seriously in error and estimate the correct value.

Corrected to 760 mm. by the Hass-Newton equation this becomes 161°/760 mm. The boiling point of 1,3-dichlorobutane is given correctly in the literature as 134°C. This isomer differs from 1,3-dichloro-2-methylpropane in just the same way that 2-chlorobutane differs from 1-chloro-2-methylpropane since in both cases the dichloride may be formed from the monochloride by substituting a hydrogen of the methyl group two carbon atoms distant from the first chlorine atom.



The boiling points of the monochlorides show that there should be something like 0.6° between the boiling points of the dichlorides. 134° + 0.6 = 134.6° for the estimated b. p. of 1,3-dichloro-2-methylpropane. Very careful determinations on this compound after repeated recrystallization from liquid propane have shown that it boils at 136.0°/760 mm. The boiling point at 10 mm. is not 45° but 24.5°.

Problem 5. The value given in the literature for the boiling point of 1,4-dichlorobutane is 163°. Show that this is too high and estimate the correct value.

The boiling points of the homologous alpha-omega dichlorides of the normal paraffins are as follows:

Compound	*B. P.*	*B. P. Increment*
CH_2Cl_2	41.6	
		42.9
$C_2H_4Cl_2$	83.5	
		36.9
$C_3H_6Cl_2$	120.4*	
		42.6
$C_4H_2Cl_2$	163 (incorrect)	
		19.3
$C_5H_{10}Cl_2$	182.3	

It is evident that one or the other of the last two values is seriously in error. The possibility that the value for 1,5-dichloropentane is considerably erroneous is eliminated by the fact that it is so close to the known value (178°) for $\beta\beta'$-dichlorodiethyl ether, since aliphatic ethers containing four or more carbon atoms in which the ether oxygen is not a part of a ring invariably boil close to the corresponding compound derived by substituting a CH_2 group for the ether oxygen. The following additional examples illustrate this:

$CH_3·CH_2·O·CH_2·CH_3$ b. p. 34.5°	$CH_3·CH_2·CH_2·O·CH_3$ b. p. 37°	$CH_3·CH_2·CH_2·CH_2·CH_3$ b. p. 36°
$CH_3·CHCl·O·CH_2·CH_3$ b. p. 98°	$CH_3·CHCl·CH_2·CH_2·CH_3$ b. p. 96.7°	
$CH_3Cl·CHCl·O·CH_2·CH_3$ b. p. 145°	$CH_3Cl·CHCl·CH_2·CH_2·CH_3$ b. p. 143°	

A redetermination of the boiling point of 1,4-dichlorobutane showed it to be 155.0/760 mm., the value reported in the literature being presumably due to a misprint or mistake in copying notes.

* Often given incorrectly as 125°.

The increments for each additional CH_2 group in the alpha-omega dichloroparaffins are now as follows: 41.9, 36.9, 34.6, and 27.3. This series thus shows the usual continuous decrease in the boiling-point increment as we ascend the series.

Problem 6. The literature shows two values for 2-methyl-1-nitropropane. These are 158–9° and 137–40°C. Show which one is more nearly correct.

The boiling point of 1-nitrobutane is 151°. Isobutyl derivatives invariably boil lower than the corresponding normal isomers. The following examples illustrate this:

n-Butyl chloride, 78.50°	Isobutyl chloride, 68.85°
n-Butyl alcohol, 117.7°	Isobutyl alcohol, 107.3°
n-Butyl acetate, 126.5°	Isobutyl acetate, 118.3°

The boiling point of 2-methyl-1-nitropropane can therefore be estimated as being about 10° lower than the normal isomer or 141°. An accurate determination showed 140.5°.

Problem 7. There has been a great deal of controversy in the literature as to whether 1-pentene is the isomer boiling around 30° or the one boiling around 39–40° (*8*). Show that this disagreement would never have arisen if boiling-point data had been properly considered.

The following data have long been available:

Ethane	−88.3°	Ethylene	−103.8°	Difference	−15.5°
Propane	−44.5°	Propylene	−47.0°	Difference	−2.5°
Butane	+0.6°	1-Butene	−5.0°	Difference	−5.6°
Pentane	+36.2°	1-Pentene			

The olefins with the double bonds between carbon atoms 1 and 2 always boil lower than the corresponding paraffins by a value which averages about 8°. 1-Pentene should therefore boil close to 28° and the lower value is the correct one.

The very thorough and excellent researches of Dr. Boord and students have shown that the boiling points of all the olefins may be correlated under a few simple generalizations.

The above illustrations serve to indicate the general procedure. While the examples chosen have been confined to aliphatic compounds, the method works equally well with aromatics and alicyclics. The accuracy of the prediction depends upon the existence of reliable data in the literature for closely analogous or homologous compounds, but if such information is available the result is never in error by more than a few degrees. It seems obvious that the general adoption of such a means of checking laboratory results—empirical though it is—would prevent the inclusion of most if not all of the erroneous boiling-point data which are at present accumulating in the literature.

ACKNOWLEDGMENT

The writer wishes to thank Messrs. Paul Weber, E. T. McBee, G. E. Hinds, E. B. Hodge, and R. K. Toner, who have obtained or checked the boiling points used in this paper.

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CORRESPONDENCE

EXPLOSION HAZARDS FROM THE USE OF ISOPROPYL AND OTHER ETHERS

To the Editor

DEAR SIR:

In the August issue (*1*), isopropyl ether was recommended as a suitable extraction medium. Subsequently, the author has had his attention called to correspondence by Morgan and Pickard (*2*) in which they cite two explosions which resulted from the use of this solvent. In each case the ether had stood for a period of five or six years and peroxides had accumulated. Quoting from their article,

> Diisopropyl ether had been employed to extract small quantities of organic acids from an aqueous solution, and after drying, about 50 cc. of the extract was distilled with the aid of an electric heater. After practically all the ether had passed over white fumes were noticed and the heater was switched off. A few moments later the explosion occurred and the worker received numerous glass fragments in the hands and face but sustained no serious injury although one lens of his spectacles was shattered into fragments and the other was pitted....
>
> It is abundantly evident that the greatest care should be exercised in every operation involving the application of diisopropyl ether. The inference may be drawn that freshly prepared diisopropyl ether can be distilled from a water bath without danger, but that, on keeping, it is liable to develop quantities of peroxides and to become dangerous....
>
> Old specimens and those of doubtful age should never be used unless they fail to liberate iodine from aqueous potassium iodide.

This warning against the use of aged ethers is extended by Williams (*3*) as follows:

> All ethers which we have studied have been found to form peroxides upon storage, and with practically all, explosions have been experienced. Diethyl, ethyl tertiary butyl, ethyl tertiary amyl, and diisopropyl ether are very hazardous....
>
> Diethyl ether is well known to form explosive peroxides....
>
> Danger occurs whenever an ether is dry distilled, usually toward the end of the distillation as the peroxide concentration increases. How far one can go with the distillation depends upon the amount of peroxide present; mechanical shock increases the likelihood of explosion. No ether should be dry distilled unless peroxides have been proved absent. Even a trace of peroxide may be dangerous since it becomes concentrated in the still residues.
>
> Peroxides are determined by adding acidified alcoholic potassium iodide and titrating the liberated iodine with thiosulfate.
>
> Peroxides are destroyed by treatment with ferrous sulfate, sodium bisulfite, acidified potassium iodide, or sodium sulfite. The latter reacts more slowly and less completely than the others. When the peroxide content is high, treatment may evolve considerable heat and the reagent should be added slowly and with cooling....
>
> The development of peroxides during storage may be considerably retarded by the addition of oxidation inhibitors. Suitable inhibitors are diphenylamine, α-naphthol, β-naphthol, and hydroquinone.... Approximately 0.05% of the inhibitor is added. Though these inhibitors are effective in reducing peroxide formation to perhaps one hundredth of that which would be formed without an inhibitor, it is advisable not to trust them implicitly but always to test for peroxides and destroy them if found before distillation, and then, if convenient, to distil the ether with steam.

Upon testing our stock of ethers, it was found that they all contained traces to appreciable amounts of peroxides. Butyl ether which had been in stock a little over a year gave a very positive test for peroxides. Our Store Room Department has arranged, therefore, to label all ether bottles as follows:

> BEFORE USING
>
> test this ether for explosive peroxides by shaking 1 cc. with an equal volume of a 2% solution of potassium iodide which has been slightly acidified. If iodine is liberated, purify before using.
>
> For purification, add one volume of 25% sodium hydroxide to 200 volumes of ether and steam-distil. The peroxides will be concentrated in the aqueous layer and should be poured down the drain. Test the distillate before using to insure the absence of peroxides.
>
> Peroxides are formed when ether is permitted to stand in contact with air, and should be tested for periodically.

Isopropyl ether which gave a decided test for peroxides failed to indicate the presence of peroxides after being subjected to the treatment prescribed above.

To the writer's knowledge, no explosions have occurred in regular instructional laboratories from the use of ethers in extractions. This is doubtless due to the facts that dry distillations are seldom, if ever, resorted to in the usual laboratory preparations, and departmental supply rooms do not normally carry sufficient amounts of ethers to permit them to age on the shelves long enough to become dangerous. Because of these facts, perhaps, the current laboratory manuals fail to give adequate, if any, warning relative to the possible presence of peroxides in ethers and the attendant dangers. Gattermann and Wieland (*4*), on the contrary, warn that:

> When evaporating large amounts of impure ether which has been exposed to air for a long time, the possibility of the occurrence of a violent explosion at the end of the evaporation, due to the presence of peroxides, must be taken into account. Such ether has a pungent odor, and liberates iodine from an acid solution of potassium iodide. The peroxides can be destroyed by shaking with a weakly acid solution of ferrous sulfate.

Perhaps over-emphasis has been placed on the fire hazard involved in the use of ethyl and other low-boiling ethers, and insufficient warning has been given relative to the coëxistent peroxide hazard (*5*).

Cordially yours,

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ABSTRACTS

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KEEPING UP WITH CHEMISTRY

Potato starch a "chemurgic" possibility. C. A. Brautlecht. *Chem. Industries*, **38**, 465–8 (May, 1936).—Potato-starch production was started about a century ago in the United States. Then "starch" meant potato starch. In time, corn starch began to be produced, not in many small plants, but in relatively large units with modern equipment and good control. This closed up most potato-starch plants in the country until what is left of the industry is in Aroostook County, Maine. Here too, it may eventually disappear unless the industry is modernized. Only nature, which has favored Aroostook as a potato country, has allowed its starch industry to continue when other units in Minnesota, Wisconsin, and Michigan ceased to exist. It is of interest here to note that during the past decade there has been a marked increase in potato-starch production in Canada.

In 1909, United States potato-starch production was about 25,000,000 pounds, while imports were about 12,500,000 pounds; in 1931, domestic production was about 16,000,000 pounds, while imports were about 18,000,000 pounds, largely from Germany and the Netherlands. German annual production is quite constant at about 220,000,000 pounds. Other European countries and Japan are large producers of potato starch. United States imports averaged about 16,000,000 pounds annually during the past ten-year period. The old tariff on potato starch was 2.5 cents per pound. This was reduced in December, 1935, to 1.75 cents per pound, which would probably not have much influence on domestic production, especially if both production efficiency and quality are improved.

The Aroostook potato-starch plant is one of relatively low efficiency in comparison with plants in Europe and elsewhere, where production costs are also less per ton. Low cost of corn and cassava starch is largely due to efficient extraction with modern equipment. In Aroostook, relatively little machinery is used, largely of the type developed abroad during the early history of the industry. Aroostook plants can meet some competition largely on account of potato supply and location near streams which supply water and remove waste.

This potato-starch industry is of importance in Maine but is little known or appreciated in general. When examined from several viewpoints, it can be concluded that: (*a*) the United States is so situated from the agricultural, industrial, and scientific viewpoint, a "chemurgic" viewpoint, that it can economically sustain a potato-starch industry, and that (*b*) the Maine potato-starch industry can and should be further developed.

A. T. B.

British researches for a new alcohol motor-fuel blend. C. H. S. Tupholme. *Chem. Industries*, **38**, 469–70 (May, 1936).—At the Billingham coal hydrogenation plant, according to published figures, for one ton of gasoline produced, 1.6 tons of coal (ash-free dry basis) must be hydrogenated, and a further 1.55 tons is required for steam and gas production, a total of 3.15 tons or, allowing for ash and moisture, 3.65 actual tons. This is equivalent to 82 gallons of gasoline from one ton of coal used. According to published estimates, the cost of production, including capital charges, is $7\frac{1}{2}$ d. per gallon, which is double the C. I. F. cost of imported gasoline. Plainly, the process must necessarily remain for a very long time uneconomic.

However, a new line is being actively pursued by an important coal-mining group in Britain with the object of producing methyl alcohol from coal. Research and experimentation have been carried on for four years and a plant, details of which cannot yet be published, is being erected to operate on commercial lines.

Last year, 47,185,108 gallons of ethyl and methyl alcohol was produced in Britain. The raw materials consisted chiefly of malt, unmalted grain, rice, and molasses. It is claimed that by the process now being operated methyl alcohol can be produced from coal at a fraction of present costs. Laboratory tests indicate that the recoverable methyl alcohol from one ton of coal is 246 gallons. Reactions required heat to convert the water and carbon into a gas, and for every ton of coal processed an additional three-quarters of a ton is used for producing the necessary heat, so that the actual liquid alcohol produced from every ton of coal used is 140 gallons.

Methanol used by itself as motor fuel requires higher compression in an engine to obtain those super-results which make it attractive for racing. The thermal efficiency of methyl alcohol with high compression ratios is greater than gasoline, but with standard compression gives fewer miles to the gallon. Best results in ordinary motor use are obtained when methyl alcohol is mixed with benzene in a 40:60 ratio, or with gasoline in a 20:80 ratio.

The research referred to seeks to retain the advantages of methyl alcohol without having to resort to mixing with benzol or other spirits. In other words, the highest accomplishment would be a spirit commanding popular use by a self-contained system.

Methanol is an active solvent of heavy hydrocarbon gases; for instance, one volume of alcohol will dissolve from 12 to 15 volumes of butylene at ordinary pressures. Ethylene, and also the saturated gases propane, butane, and ethane, are soluble in alcohol. A solution of these heavy gases in alcohol constitutes an excellent motor fuel which permits starting an engine with ease even in cold weather, besides giving elasticity and excellent acceleration in running. These gases held in alcohol show but little tendency to escape. The solution has a much lower flash point and initial boiling point than is possessed by alcohol alone, and a greater thermal value. The product also has larger fractions volatile at low temperatures.

If, before processing the raw coal for methyl alcohol production, this coal, as well as the coal used for heating, is submitted to preheating whereby 80 per cent. of the volatiles are released (with the minimum of methane and ethane and the maximum of the heavy hydrocarbons), this yields a supply of hydrocarbons for solution in the alcohol, affording the particular requirements of a self-contained motor spirit. A. T. B.

Modern explosives—II. S. I. Levy. *Sch. Sci. Rev.*, **17**, 488–500 (June, 1936).—Before the war the high explosive most commonly used for shell-filling was picric acid. During the war trinitrotoluene came into extensive use for this purpose. Other aromatic nitro-bodies, used either alone or mixed with T. N. T., lead nitrate, and ammonium nitrate, were dinitrobenzene, dinitronaphthalene, and trinitrophenylmethylnitramine. The aromatic nitro-compounds do not contain sufficient oxygen for their combustion, thus giving rise to dense clouds of black smoke on detonation. They are therefore mixed with substances such as ammonium nitrate, which contain enough oxygen to afford complete combustion. Such mixtures are known as "smokeless" powders. Methods for the technical manufacture of picric acid, T.N.T., and ammonium nitrate are described in detail. S. W.

Manufacture of glass. M. Parkin. *Sch. Sci. Rev.*, **17**, 501–9 (June, 1936).—A discussion of the history and technology of glass manufacture. S. W.

Bromine from sea water. F. A. Philbrick. *Sch. Sci. Rev.*, **17**, 521–5 (June, 1936).—A digest of an article in *Industrial and Engineering Chemistry*, **26**, 361 (1934). S. W.

Sword oil. Anon. *Ind. Bull. Arthur D. Little, Inc.*, **114**, 1 (July, 1936).—The whole field of fish oils is under investigation today as vitamin sources, the "big three" being cod, halibut, and swordfish. The swordfish, that ferocious, warm-water food fish, provides the most concentrated natural source of vitamins A and D. A fisheries company of Gloucester now produces this relatively scarce and valuable oil. Halibut-liver oil has been available commercially for about seven years. It is also produced in Gloucester and is inferior only to swordfish oil as a vitamin source.

The father of all vitamin-bearing fish oils is cod-liver oil, and still by far the most important oil of its class. The hake, cusk, haddock, pollack, related to the cod, are also sources of liver oil, but not equal to the cod. Sardine oil is known to have some value, and salmon oil and tuna-fish oil are achieving some recognition. Sardines and salmon yield oil from the entire body, while tuna-fish oil comes only from the liver. The production of fish-liver oils for vitamins is still an infant industry in the U. S. Incidentally, we must think more of our chickens than we do of ourselves, for they consume the greater part of the cod-liver oil sold in this country. G. O.

From submarine farms. ANON. *Ind. Bull. Arthur D. Little, Inc.*, **114,** 1–2 (July, 1936).—Seaweed is likely to assume an increasing importance in industry due to the production of alginates from a species of brown algae or kelp. Alginates were first commercially introduced in this country during the World War. During the past few years, research and development have produced substantially pure and uniform alginates as protective colloids or stabilizers in several industries. Sodium alginate is used today as an anti-settling agent for chocolate milk drinks; as an alternative for gelatin in ice-cream manufacture; and as a protective colloid and thickening agent in cosmetics and pharmaceuticals, can-sealing compounds, and boiler compounds. Sodium alginate is now being introduced to the textile industry as a tragacanth substitute in textile printing and padding, and as a gelatin substitute in slasher sizing. Tragacanth is a gummy exudation from trees and shrubs. Ammonium alginate is used principally to stabilize rubber latex. For most of the uses cited prices tend to be competitive. G. O.

A diamagnetic personality. ANON. *Ind. Bull. Arthur D. Little, Inc.*, **114,** 2–3 (July, 1936).—Bismuth, with its odd properties, is the "personality" of this article. Of late it has been playing a useful part in the scientific investigation of the properties of metals, or the riddles of their behavior and structure. Long neglected, bismuth is only now finding uses for itself and its alloys; and despite its limited supply, it has for many decades been able to exceed the demand. In its magnetic properties, it is indeed a queer actor, for it is the most diamagnetic metal of all; that is, most repelled by magnets; but alloys of bismuth with copper, another non-magnetic metal, are distinctly magnetic. Molten bismuth is found to be more than twice as good a conductor of electricity as the solid form, the opposite of most metals. In thermoelectric properties, bismuth is remarkable. But by far the chief use of bismuth is in the form of its compounds because of their medicinal nature. Its alloys are well known. Bismuth may be electroplated, and the films are capable of high polish, or may be heat-treated to produce colors. G. O.

Alcohol as motor fuel. ANON. *Ind. Eng. Chem., News Ed.*, **14,** 4277–8 (1936).—The subject of the use of power alcohol is much discussed at the present time, and both opponents and proponents use the same data to prove their points. A summary of the state of affairs in various foreign countries is presented in condensed form. A table of alcohol consumed in motor fuel for 17 countries is given. None was used in 1934 in Argentina, Australia, China, or the Philippines. The other consumptions range from 433,500 gallons in the United Kingdom to 54,400,000 gallons in France for 1934. Those countries whose petroleum supplies are low or non-existent have turned toward domestic sources of motor fuel, and alcohol produced from agricultural crops looms large in the fuel supply of farming countries. In Latin America the question of alcohol-gasoline motor fuel has received little attention. Norway uses none but Sweden provides for blending of 20% alcohol. Austria, Czechoslovakia, Hungary, Jugoslavia, Latvia, and Poland have utilized alcohol and cut down petroleum importations. France, Germany, and Italy have used every effort to force the use of substitutes for petroleum and Italy has a law effective January 1, 1938, requiring that all passenger cars must be powered with gas or other domestic fuel. In Hungary gasoline used by all taxi and bus companies is blended with 20% of anhydrous alcohol. Corrosion is prevented by the use of alloys and no damage to motors is reported. The use of alcohol as a motor fuel is unimportant in Japan but the government of Manchuria is planning a monopoly of use of fuel alcohol. With the exception of Cuba and the Philippines, each country using large quantities of fuel alcohol has encouraged it by some legislative action. In general, satisfaction with the blended fuels is reported. Where price differentials exist between blended and non-blended fuels, the equalization is brought about by taxes or compulsory use of blended fuels. This trend in the use of alcohol as a fuel seems to come largely from the desire to be free from foreign supplies as much as possible.
A. A. V.

Commercial demonstration to test power alcohol feasibility. H. G. HULL. *Chem. & Met. Eng.*, **43,** 352–4 (July, 1936).—America's first power alcohol plant is located at Atchison, Kansas. It has a rated capacity of 10,000 gallons per day. Requests and orders so far have exceeded this capacity by four times. Standard equipment and reactions are used in the manufacture of the alcohol itself. Experiments are being carried out with the use of diethyl ether as a final dehydrating agent. The ether reacts with the water, in the presence of a catalyst, to give alcohol itself.

Denaturing is one of the thorns in the side of the power alcohol forces. The denaturant must be economical, effective, and as good a fuel as the alcohol itself. Much progress has been made toward this goal. J. W. H.

Handling and shipping of hydrofluoric acid. G. CHURCH. *Chem. & Met. Eng.*, **43,** 366–8 (July, 1936).—Bought for its ability to attack glass and metal, hydrofluoric acid becomes by this very characteristic one of the most difficult chemicals to keep confined, since shipping containers for liquid acids are usually of one or the other of these materials.

If the acid is 30% or less, the wooden barrel is the most economical container. The barrel must be lined with pitch before use and rough handling often breaks this lining. A wooden barrel cannot be used for storage for more than 60 days.

Boxed lead carboys have been much used for acid of greater than 30% concentration. They are subject to injury from rough handling and must be carefully inspected after each trip. A carboy will not stand more than a dozen trips.

A steel container has been found quite practical for 60% acid. It is first coated on the inside with iron fluoride. But rough handling may break this coating and cause trouble. Steel drums must also be shipped and stored on their sides in order to keep the acid from eating away the bung.

The most recent container is a rubber drum. It needs no steel hoops, no special lining, no crating. It is not subject to leaks and can be handled in an upright position. Larger rubber drums are now needed. J. W. H.

Yeast from wood. E. W. EWESON. *Chem. Industries*, **38,** 573–4 (1936).—About six months ago, operations began in a new chemical operation linking together two so fundamentally different industries as sulfite pulp and yeast manufacture. Close to 20,000 pounds of baker's yeast per week is produced at the Liverpool, Nova Scotia plant of Best Yeast, Ltd., and additional equipment to double this production capacity is now being installed. It would appear that a new solution of the pulp industry's waste problem is thus presented.

In the manufacture of baker's yeast, a pure cultivated yeast is used as starting material, and for bread-making the strain employed consists solely of *Saccharomyces cerevisiae*. This yeast, the so-called seed-yeast, is supplied with nutrition which consists chiefly of carbohydrates in the form of sugar. Formerly, malted cereals were used for this purpose. This was a complicated, tedious process which frequently resulted in anything but a pure yeast. Subsequently came the use of molasses, which also is not of a pure nature. Recently utilization of the sugar of sulfite liquor in the manufacture of yeast has been successful.

The waste liquor in the sulfite mills from cooking wood, mostly spruce and hemlock, under pressure in digestors with calcium bisulfite and water, contains all the lignin in the wood and also about 2 to 3 per cent. of sugar; in all, about 10 to 12 per cent. of solid matters. The sugar goes into solution in the liquor during the cooking process and reaches a maximum concentration in the latter part of the cooking of about 3 to 3.5 per cent. when the liquor has a temperature of 130 degrees to 140 degrees C.
A. T. B.

Materials for chemical pumps. C. H. S. TUPHOLME. *Chem. Industries*, **38,** 575–6 (1936).—Pumps concerned with ordinary duties and less difficult fluids may be considered as based, for constructional purposes, on the cast iron-steel-gunmetal-bronze range of materials. But departures through policy, specification, and necessity are numerous.

The cast iron applies generally for the casings, although it may become the metal for all parts in handling alkaline liquids. Gunmetal may displace cast iron for casings in salt water uses, though monel metal is used because of its resistance to sea water and to brines encountered in industrial processes. The gunmetals and bronzes apply, with Admiralty gunmetal and phosphor bronze predominating, for such parts as liners, rotors, and valves. Steel and bronze are used for pump rods and spindles.

Variations of grade and combination within these classes of materials are extreme, but departures from the general groups are of most significance. These departures have, in most cases,

a tendency toward the nickel-alloy steels and the copper-nickel alloy groups. A. T. B.

Lead burning practices in the repair of chemical equipment. E. B. PARTINGTON. *Chem. Industries*, **38**, 605–7 (1936).—Lead burning (lead welding) has of necessity to be used very extensively in the repair and maintenance of chemical equipment owing to the fact that both sheet and lead pipes are used in large quantities for chemical plant construction. Plumbers' solder, moreover, is not satisfactory for jointing lead that is to be used for either the conveyance or storage of acids because the tin in the solder is readily attacked and joints are thus made porous; therefore, it is necessary to make all connections between two or more pieces of lead by "lead burning." A. T. B.

APPARATUS, DEMONSTRATIONS, AND LABORATORY PRACTICE

Chemiluminescence. R. P. AYRES. *Sch. Sci. Rev.*, **17**, 615 (June, 1936).—The following chemiluminescence experiments are described.

1. Ozone on safranin. A solution of safranin in alcohol (25 g. per 100 cc.) is placed in a Woulff bottle and sprayed into an inverted wide-mouthed 500-cc. flask, where it comes in contact with ozonized air and gives a brilliant fluorescence.

2. Hydrogen peroxide on a pyrogallol-formaldehyde mixture. The following solutions are made up.

10% pyrogallol in water
40% potassium hydroxide
40% formaldehyde
30% hydrogen peroxide

A mixture of 50 cc. pyrogallol, 50 cc. potassium hydroxide, and 35 cc. formaldehyde is placed in a tap-funnel, and the hydrogen peroxide, in a second funnel; both funnels are inclined over an ordinary filter-funnel or glass spiral. The rates of flow of the two solutions can be adjusted to give a brilliant red glow. S. W.

The Kuder colorimeter. ANON. *Laboratory*, **8**, 4–7 (1936).—Complete elimination of the personal element in color evaluation, by replacing the human eye with an electric one, a stable photoelectric cell is one of the important features in the new Kuder colorimeter. Combined with this is another development in analytical tools—this instrument is provided with standardized scales which can be read directly in units of the unknown ingredient being determined.

Another feature is the fused one-piece pyrex glass fluid cell. This cell will withstand any chemicals which do not affect pyrex glass. A. T. B.

Make-up for the graduate. ANON. *Laboratory*, **8**, 14 (1936).—Anemic old graduates, burets, thermometers, pipets, and similar appliances can be restored to their original beauty and usefulness by an application of the Fisher Graduate Filler. This compound, which is highly resistant to chemical action, will restore the old, faded graduation marks. A. T. B.

Prescription chemistry. E. ALTMAN. *Rept. New Eng. Assoc. Chem. Teachers*, **148**, 170–85 (May, 1936).—Outlines necessary training for a pharmacist and allied professions. Directions are given for the preparation of a typical plaster, a pill, and an ointment. The application of thorough knowledge is shown to be necessary in the compounding of prescriptions. "Five hundred drugs or preparations will make 275,838,552,475 different combinations, using from one to five items in each combination." S. G.

ADMINISTRATIVE PROBLEMS AND DEVICES; CURRICULA

The new examination program in science of the College Entrance Examination Board. A. KLOCK. *Rept. New Eng. Assoc. Chem. Teachers*, **148**, 167 (May, 1936).—The new program seeks to emphasize power to use facts, rather than the memorizing of isolated facts in science teaching and examinations. The present syllabus covers too much ground. Integrated courses in science now being developed in some schools call for examinations at different levels. The Board, in seeking to cover this need, is urged to offer first-level examinations in biology, chemistry, physics; second-level, biological sciences, physical sciences; third-level, biology, chemistry, physics—including mathematics gamma. Sample questions of the comprehensive type are given along with aims in teaching science. S. G.

Problems of the Master's degree. Report of the Committee on the Master's Degree presented to the Association of American Universities. WILLIAM J. ROBBINS, Chairman. *J. Higher Educ.*, **7**, 265–7 (May, 1936).—There is an increasing tendency to establish new Master's degrees. This Committee reaffirms the principle contained in the report of the Committee on Academic and Professional Higher Degrees:

1. The multiplication of degrees is to be avoided.
2. A Bachelor who completes a second baccalaureate curriculum should receive a second baccalaureate degree rather than a Master's degree.
3. In appropriate cases the M.A. or M.S. may be supplemented by a qualifying phrase.

The Committee recommends that the administration of the Master's degree be centralized in the graduate school, with due care that the group interests are properly represented and sympathetically heard. It is of the opinion that the division of the administration among schools or departments may result in lowering standards and may artificially restrict the combination of subjects that students may pursue by the development of barriers along college or departmental lines. A. T. B.

PROFESSIONAL

Whither engineers and engineering education? W. N. JONES. *Chem. & Met. Eng.*, **43**, 310–2 (June, 1936).—Contrary to popular but uninformed opinion, men who have shown serious scholastic attainments in college obtain better positions and greater financial reward than men who have shown mediocre ability in the classroom. The following characteristics determine the future of the individual engineer: fundamental and well rounded engineering training, shop experience, good, pleasing, serious, and acceptable personality, ability to work with others, ability to write logical letters and reports, ability to read German, participation in extra-curricular activities, analytical-mindedness, ingenuity, determination, stability, poise, accuracy, companionship, designing ability, mechanical ability and aptitude, good character, good health, neat appearance and good address, willingness to assume responsibility, fluency in spoken English, wide range of interest, mental alertness, creative ability, initiative, industry, courage, aggressiveness, tenacity, dependability.

The author feels it would pay more engineers to go on with graduate work and predicts engineering schools and industrial research departments will demand such training for their staff members in the future. J. W. H.

FOREIGN CHEMICAL AND EDUCATIONAL CONDITIONS

Chemical engineering education in Switzerland. H. E. FIERZ-DAVID. *Chem. & Met. Eng.*, **43**, 264 (May, 1936).—Switzerland has seven universities and one institute of technology, in all of which chemistry is taught as it is the world over. But only at the Institute of Technology at Zürich is special emphasis placed on other than simon-pure chemical instruction. Two professors at the Institute are occupied exclusively with the technical and commercial aspects of chemistry. Fully 95% of the Institute's graduates go on to other institutions to earn their doctors' degrees. J. W. H.

The progress made by the German chemical industry in 1935. B. WAESER. *Chem.-Ztg.*, **60**, 57–8 (Jan. 15, 1936).—A survey. L. S.

The development of the British chemical industry in 1935. T. W. JONES AND N. W. VERE JONES. *Chem.-Ztg.*, **60**, 66–7 (Jan. 18, 1936).—A survey. L. S.

Survey of the supply of metals and ores in Germany. E. KORDES. *Chem.-Ztg.*, **60**, 53–5 (Jan. 15, 1936) and 73–5 (Jan. 22, 1936).—A survey dealing with iron, steels, copper, lead, zinc, tin, aluminum, and other light metals. L. S.

RECENT BOOKS

INTRODUCTION TO THEORETICAL CHEMISTRY. *William Buell Meldrum*, Professor of Chemistry, Haverford College, and *Frank Thomson Gucker, Jr.*, Associate Professor of Chemistry, Northwestern University. American Book Company, New York City, 1936. xiv + 614 pp. 155 figs. 15 plates. 14 × 21.5 cm. $3.50.

The book is designed for students in their second year of chemistry. It has been used in connection with courses in qualitative and quantitative analysis by the authors. It is intended to enable the student to obtain a comprehensive knowledge of the fundamental generalizations and theories of chemistry. The scope of the book is best indicated by the titles of the chapters: The Elements and Their Classification; Chemical Combination and the Atomic Theory; The Gas Laws and the Kinetic Theory; Solutions; Fundamental Chemical Theory; Thermochemistry; Reaction Velocity and Equilibrium; Arrhenius' Theory of Ionization; Reactions According to the Ionic Theory; Quantitative Applications of the Ionization Theory; Neutralization Indicators; Electrical Conductance; Electrode Effects; Electromotive Force; Applications of Electrode Potentials; Modern Theories of Electrolytes; Radiations and Spectra; Radioactivity; Isotopes; Atomic Structure—The Nucleus, Transmutation of the Elements; Atomic Structure—Arrangement of the External Electrons; The Electronic Theory of Valence.

The work is about as comprehensive in its treatments of the different topics as is possible without the use of the calculus. It is well written and should be understandable to second-year college students. Those who cover the work should certainly be well prepared for the more advanced courses in chemistry. It contains good treatments of the applications of oxidation potentials, the equilibrium formulation, reaction rates, etc., which are directly to the point in qualitative analysis. A large portion of the book, however, is devoted to topics which are not directly concerned with analytical chemistry. The reviewer feels that it would be difficult to correlate the laboratory work in analytical chemistry with lectures and class work based on this text and to cover the material in the text during one school year.

The reviewer cannot help but feel that the more rigorous treatment of the fundamental generalizations and modern theories which is possible with senior and even junior students with a broader background in chemistry, physics, and mathematics is to be preferred to the less rigorous treatment necessary with sophomores.

However, those who disagree with the reviewer about the time when theoretical chemistry should be introduced will find here an excellent text, conservative, but not too much so, interesting, and well suited for students who have had one year of college chemistry, one year or less of college physics, and no calculus. Exercises are provided for most of the chapters and many good references for outside reading are included.

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ANNUAL REVIEW OF BIOCHEMISTRY, VOLUME V. *James Murray Luck*, Editor, Stanford University. Annual Review of Biochemistry, Ltd., Stanford University P. O., California, 1936. x + 640 pp. 15 × 22 cm. $5.00.

"In the year that has elapsed since publication of the fourth volume of the *Review* there have been no changes in editorial or publication policy." The fifth volume comprises the following chapters.

Oxidations and Reductions. D. E. Green and D. Keilin.
Enzymes. J. H. Quastel.
X-Ray Studies on the Structure of Compounds of Biochemical Interest. O. L. Sponsler and W. H. Dore.
The Chemistry of the Carbohydrates and the Glucosides. W. N. Haworth and E. L. Hirst.
The Chemistry of the Acyclic Constituents of Natural Fats and Oils. T. P. Hilditch.
The Chemistry of the Proteins and Amino Acids. C. Rimington.
The Chemistry and Metabolism of Compounds of Sulfur. V. du Vigneaud and H. M. Dyer.
Chemistry and Metabolism of Compounds of Phosphorus. R. Robinson.
Carbohydrate Metabolism. I. L. Chaikoff.
Fat Metabolism. E. F. Terroine.
Metabolism of Amino Acids. H. A. Krebs.
Mineral Metabolism. E. B. Hart and C. A. Elvehjem.
Clinical Applications of Biochemistry. J. P. Peters, C. L. Robbins, and P. H. Lavietes.
The Hormones. E. A. Doisy and D. W. MacCorquodale.
The Water-Soluble Vitamins. H. von Euler.
The Fat-Soluble Vitamins. E. V. McCollum.
Nutrition. A. H. Smith.
Liver and Bile. A. C. Ivy and L. A. Crandall, Jr.
Comparative Biochemistry of the Vertebrates and Invertebrates. F. Kutscher and D. Ackermann.
Animal Pigments. J. Roche.
Metabolism of Carbohydrates and Organic Acids in Plants. W. Ruhland and J. Wolf.
The Biochemistry of the Nitrogenous Constituents of the Green Plants. G. T. Nightingale.
The Rôle of Special Elements (Boron, Copper, Zinc, Manganese, etc.) in Plant Nutrition. P. Mozé.
Bacterial Metabolism. A. J. Kluyver.
Soil Microbiology. S. A. Waksman.
Biochemistry of Fungi. N. N. Iwanoff and E. S. Zwetkoff.
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OTTO REINMUTH

FRONTIERS OF SCIENCE. *Carl Trueblood Chase*, Ph.D., New York University. D. Van Nostrand Co., New York City, 1936. xi + 352 pp. 19 plates. 13 × 21 cm. $3.75.

In the concluding paragraph of the introductory chapter the author sets forth the purpose and scope of the book as follows: "It is our purpose to visit each of the present frontiers of science, to see what is being done there, and to make inquiry as to the possible effect of this work on human destiny, and on man's idea of his place in a universe which at times appears to be so vast and so incomprehensible as to render the human race a thing of supreme insignificance."

The remaining nineteen chapters are grouped under the heads: Frontiers of Time and Space, The Quest for the Ultimate, The New Age of Chemistry, The Frontiers of Health, and The Secret of Life.

The whole treatment is keyed to the dramatic. On page 132 we read: "Increasing familiarity with the electron had set the stage for great discoveries. As the curtain rises, Professor Planck is hard at work with pencil and paper, seeking the solution of a puzzle. He is trying to discover why the laws of radiation are in disagreement with the results of experiment. Before the curtain falls on the last act he will have found the solution, a solution that has since 1900 provided plots for several equally exciting dramas."

Again, on page 153, in introducing the work of de Broglie, the author states: "The time was ripe for a new theory. When it arrived, its dénouement was so sudden that many physicists still find themselves gasping for breath. And the reading public, at least that part interested in the doings of the scientists, has been well nigh asphyxiated."

Another appeal to the dramatic is found on page 185 in the presentation of the controversy over the nature of cosmic rays: "Spectacular as were the discoveries made during 1932, the scientific world as well as that larger world that waits eagerly for each new announcement from its smaller neighbor was not

spared a touch of the dramatic. For it was during the closing days of 1932 that two American physicists, each a leader of thought and possessed of strong convictions, each a Nobel Laureate, came into open disagreement on a subject of fundamental scientific importance."

While the content and style of the book are designed to intrigue the scientific layman, the Editorial Committee of the Science Book Club was sufficiently impressed with its "keen appraisal and prophetic judgment" to select it as its principal recommendation for June. From the point of view of physics and astronomy the book presents as masterly an exposition in non-technical language of recent discoveries in these fields as one may find, but when the author enters the chemical and biological sciences, he fails to maintain this high standard. Indeed, the contrast is so sharp that the book offers one of the best examples of the results to be expected when a specialist in one field attempts to describe, even for the layman, present-day problems in another. The discussions of the first two sciences are not only vivid and animated, but they carry that convincing voice of authority which is found only in one who has experienced intimate contact with the phenomena presented. On the other hand, the problems selected from chemical and biological research can hardly be said to represent those that are of major significance today, and the treatment of the same is so incomplete that in comparison with the earlier discussion it appears trite, inane, and superficial. Only Eyring's theories of chemical combination are vitalized while from the chapters dealing with the life sciences, the one on Immunology is the most complete.

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A TEXTBOOK OF ELEMENTARY QUANTITATIVE ANALYSIS. *Carl J. Engelder*, Professor of Analytical Chemistry, University of Pittsburgh. Second edition. John Wiley & Sons, Inc., New York City, 1936. xiv + 270 pp. 9 tables. 12 figs. 15 × 23 cm. $2.75.

In this (the second) edition of Professor Engelder's quantitative text, volumetric analysis is made to precede gravimetric—an arrangement that seems to be of growing popularity nowadays; yet the reviewer has always felt that, while the expedient may have some advantages, it does not maintain what is obviously the logical sequence; and there are others who appear to hold a like opinion, among whom Doctors I. M. Kolthoff and E. B. Sandell may be named.

In any criticism of the work now under discussion, one's comments will depend very largely upon the standpoint from which it is judged. As an aid to young people who are essaying quantitative analysis for the first time—assuming that these pupils have no particular interest in the subject and therefore do not wish to devote much time to it, and, more especially, that they do not aspire to become proficient analysts—the book may serve its purpose reasonably well. In fact, the following educational features are distinctly meritorious: the exposition of theoretical principles as each new type of method is being approached, the detailed explanations in stoichiometry, the abundance of simple questions and problems—all of which should help toward the learner's mental development. On the other hand, when viewed practically, the treatise leaves much to be desired. In other words, it would seem that the author is not much in sympathy with Doctor G. E. F. Lundell's plea for "the chemical analysis of things as they are." The student is put to work on made-to-order samples and is given but a slight inkling of how to modify his course in case the commonly interfering substances should happen to be present, and, as is worse, the book teems with errors of omission and loose statements.

The operator is told to determine copper in a water-soluble salt by the De Haen process (pages 158–9). in a brief prelude he is advised that the disturbing elements in ores may be got rid of by deposition of the copper through the agency of metallic aluminum (the all-important details of procedure being omitted, and the convenient substitution of granulated zinc for aluminum not being mentioned), but nothing is said regarding the possible interfering action under certain conditions of oxides of nitrogen, arsenic, antimony, mineral acids, and ammonium acetate; moreover, the ingenious fluoride-phthalate-iodide method of B. Park is left out of account. It is regrettable that the apparently excellent work of R. M. Fowler and H. A. Bright at the National Bureau of Standards on the standardization of potassium permanganate solutions has passed unnoticed. It seems improbable that anybody will obtain a "colloidal precipitate" of barium sulfate (page 186). It is surprising that one should be directed to wash silver chloride with "hot water containing dilute nitric acid" (page 194), for a wash-liquid cooled in ice would be more appropriate, seeing that the solubility of the silver halide increases markedly with rise in temperature. The scheme for the analysis of brass (page 230 *et seq.*) is open to a number of objections: the stannic oxide, as weighed, is apt to be in error owing to one or more of several causes: contamination, passage through the filter, or reduction during ignition; and no provision is made for either iron or nickel, which are so frequently to be found in copper-zinc alloys. Since there is no indication to the contrary, the reader is led to suppose that the whole of the silica is recovered by two evaporations with hydrochloric acid in the analysis of a siliceous material (page 239 *et seq.*), whereas a very noteworthy amount can be collected subsequently from the precipitate produced by ammonium hydroxide (oxides of iron, aluminum, titanium, phosphorus, etc.). In the sentence beginning with "Limestone consists mainly of impure calcium carbonate . . . " (page 241) a redundancy obtains.

The figures show signs of extremely neat drafting, the typography is satisfactory, the dark red binding is attractive, and, on the whole, the book is very pleasing in appearance.

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ANNUAL SURVEY OF AMERICAN CHEMISTRY, VOLUME X, 1935. Edited by *Clarence J. West*, Research Information Service, National Research Council. Published for the National Research Council by the Reinhold Publishing Corporation, New York City, 1936. 487 pp. 13 × 21 cm. $5.00.

The current volume of the Survey comprises the following chapters:

Theories of Solution. Herbert S. Harned and Benton B. Owen.
The Kinetics of Homogeneous Gas Reactions. F. O Rice and K. F. Herzfeld.
Molecular Structure. E. Bright Wilson, Jr.
Thermodynamics and Thermochemistry. R. E. Gibson.
Contact Catalysis. L. H. Reyerson.
Inorganic Chemistry, 1933–1935. Don M. Yost.
Analytical Chemistry, 1934 and 1935. G. Frederick Smith.
Applications of X-rays in Metallurgy. Eric R. Jette.
Ferrous Metallurgy. Frank T. Sisco.
The Platinum Metals. Raleigh Gilchrist.
Electro-organic Chemistry. Sherlock Swann, Jr.
Aliphatic Compounds. M. S. Kharasch and C. M. Marberg.
Carbocyclic Compounds. W. E. Bachmann and F. Y. Wiselogle.
Heterocyclic Compounds. Guido E. Hilbert.
Alkaloids. Lyndon Small.
Food Chemistry. Caroline C. Sherman and Henry C. Sherman.
Insecticides and Fungicides. R. C. Roark.
Gaseous Fuels, 1934 and 1935. Lloyd Logan and Wilbert J. Huff.
Petroleum Chemistry and Technology. Merrell R. Fenske.
Detergents and Detergency. Pauline Beery Mack.
Cellulose and Paper. Harry F. Lewis.
Synthetic Plastics. Gustavus J. Esselen and Walter M. Scott.
Rubber. Webster N. Jones.
Unit Processes in Organic Synthesis. Edited by P. H. Groggins.
Chemical Economics (1931–1935). Lawrence W. Bass.
Author Index.
Subject Index.

OTTO REINMUTH

ORGANIC CHEMISTRY. *Robin Charles Burrell*, Associate Professor of Agricultural Chemistry, The Ohio State University. McGraw-Hill Book Company, Inc., New York City, 1936. xii + 331 pp. 34 figs. 14 × 20 cm. $2.75.

In his preface the author states that this book is designed primarily for students in home economics and that "it includes the fundamental concepts of organic chemistry," and "should be useful in many colleges and agricultural schools where a brief course in the fundamentals of organic chemistry is desired." The subjects discussed are based upon the results of a survey (by Miss Bell at Ohio State University) made to determine those principles of highest importance to students of nutrition. Those subjects relating to organic chemistry which this survey revealed as most important are dealt with in the book, the emphasis on each being based upon the results of the survey.

The book begins with a brief historical introduction and discussion of the "definition and scope of organic chemistry." Organic chemistry is defined as a study of hydrocarbons and of their derivatives. The author hopes by this definition (see pages 5 and 8) to rule out such substances as carbonic acid and its salts. This so-called "modern definition of organic chemistry" seems to us to have no advantage over the time-honored one, and to have the disadvantage of giving the student an entirely erroneous impression of the meaning of the term "derivative," for certainly carbonic acid is as much a derivative of methane as any other acid is of the corresponding hydrocarbon. In this same chapter the terms "exact chemical composition" and "molecular structure" are used synonymously. The results of studies of composition are *not* expressed, as the author claims, in the form of structural formulas, but in percentages of the various elements present.

There follows a rather detailed description of the common operations of organic chemistry, in which distillation, crystallization, analytical methods, the determination of melting points, and molecular weight determinations, etc., are considered. There is far more detail in this chapter than one would expect to find outside of a book on laboratory methods.

A chapter on structural formulas follows in which all sorts of structural isomerism are discussed, and in which is found a brief consideration of stereoisomerism. It seems to us nothing short of sheer folly to attempt to present the structural formulas of alcohols, acids, aldehydes, ethers, and the ideas of stereochemistry and unsaturation all in one brief chapter of sixteen pages. The statement (page 44) that "asymmetric molecules must contain one or more carbon atoms which are attached to four different atoms or radicals" is incorrect, and the failure to list geometric isomerism as a branch of stereoisomerism gives an erroneous impression of the scope of the latter term.

A chapter on classification of organic compounds follows, in which illustrations of the various homologous series are found, and in which organic nomenclature is discussed. In our opinion this attempt to discuss nomenclature of organic compounds as a whole will confuse the student who has not studied organic chemistry before and will make the whole subject appear hopelessly complex.

There follow chapters on hydrocarbons (open chain and cyclic), oxy derivatives of acyclic hydrocarbons (alcohols, aldehydes, and ketones), structural anhydrides of acids and alcohols (acyl chlorides, acid anhydrides, esters, ethers, alkyl halides), fats and lipids, derivatives of acyclic hydrocarbons which contain more than one characteristic atom or radical (including stereoisomerism), carbohydrates, nitrogen-containing compounds, proteins, derivatives of cyclic hydrocarbons, and natural products of complex or imperfectly known molecular configuration. Unfortunately, the author uses the terms configuration and structure synonymously throughout the book.

Following is an appendix containing a list of common terms with their pronunciations, a section in which the various principles of organic chemistry are weighed according to the survey mentioned above, a list of names of organic substances which occur most frequently in the literature of foods and nutrition, other information concerning the survey, and a list of reference books.

There are a number of errors which should be mentioned: propionitrile is called ethyl nitrile (p. 115), and a similar error occurs on the next page where the term "hexyl nitrile" is used; the definition of refractive index (page 131) is incorrect; ergot is a fungus which grows on rye, not barley; the formula of cystine (p. 213) is incorrect; and there is a typographical error in the name of alanine in Figure 27; synthetic proteins (p. 233) have not been prepared as stated (p. 233); and the inference that all vat dyes yield colorless reduced soluble forms (p. 258, line 29) is incorrect.

The sections on fats, carbohydrates, nitrogen-containing derivatives, and natural substances are by far the best chapters in the book and possess real merit; the other chapters are so brief as to be almost sketchy. One would naturally expect particular emphasis on subjects related to the chemistry of nutrition, but it seems to us that for a thorough understanding of the relatively complex substances in this field a more adequate consideration of simpler compounds would be desirable.

After a careful reading of the text the writer is of the opinion that Dr. Burrell has been too much influenced by the results of Miss Bell's survey and has devoted too little attention to an accurate, logical, and teachable development of his subject. The result is a volume which contains chapters of a high degree of excellence, and others which are distinctly mediocre, all combined in an arrangement which leaves a great deal to be desired.

Print, paper, and binding are excellent.

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ELECTROLYTIC OXIDATION AND REDUCTION: INORGANIC AND ORGANIC. *S. Glasstone*, Lecturer in Physical Chemistry, University of Sheffield, and *A. Hickling*, Assistant Lecturer in Chemistry, University College, Leicester. Vol. IX of a series of Monographs on Applied Chemistry. D. Van Nostrand Co., Inc., New York City, 1936. ix + 420 pp. 31 figs. 14 × 21.5 cm. $9.50.

During the past decade there has been a revival of interest in electrolytic oxidation-reduction processes for industrial purposes. This field was actively investigated thirty or forty years ago, but by no means exhausted. Judging by the papers published and patents registered, scientific interest is somewhat revived. Venerable topics, like overvoltage, are acquiring the new dress of quantum theory.

This monograph treats inorganic and organic reactions in their technical and scientific aspects; a serious attempt is made to elucidate the principles underlying these reactions for the benefit of research workers and technical chemists.

The first three chapters (94 pages) are devoted to a clear and concise presentation of the fundamental theory underlying Reversible Electrode Potentials, Polarization and Overvoltage, and Diffusion Phenomena in Electrolysis. Much of the material of these chapters, and the one following on Reversible Inorganic Oxidation-Reduction Processes, is to be found in many of the more comprehensive physical chemistry and electrochemistry texts.

Relatively more new material is to be found in the four chapters dealing with the less simple, but technically important topics of Irreversible Organic and Inorganic Reduction and Oxidation Processes, followed by chapters on The Polymerization of Anions, the Oxidation of Fatty Acids and their Salts, and Anodic Substitution.

The authors have been active in research in these fields and are well qualified to present the subject. There is evidence of careful and exhaustive preparation. The documentation mentions both scientific and patent literature, and should interest both technical and non-technical students.

The printing, format, and index merit favorable comment. The style is easy, and the book should find a place as a text in electrochemistry courses.

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It is important to note: First, the complete coverage with respect to all inorganic substances and all organic compounds with one and two carbon atoms. Second, the self-consistent nature of the values of heats of formation.

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TRADE ANNOUNCEMENTS

Efficient Colored Light Developed

A new kind of lamp, developed in the research laboratories of the *Westinghouse Lamp Company*, changes invisible ultra-violet radiations into visible colored light at intensities from 50 to 120 times greater than by present-day methods. The phenomenon of fluorescence, by which invisible radiations of short wave-length are transformed into visible light, is the secret of this new invention.

"A small globule of metallic mercury is vaporized by electricity until it fills a long, slender tube with a dull glow which is rich in ultra-violet radiations," explains Dr. Roy D. Hall, Westinghouse engineer. "Profuse ultra-violet radiations from this arc strike the inside surface of the tube where a coating of chemical powder transforms them into visible colored light."

Research into this new method of light production to date has been confined to the lumiline shape of bulb, the long, slender tube which is sealed at each end by a disc-like base. However, engineers envision widespread use of this type of colored light for decorative purposes when it finally emerges from the laboratory.

Grasselli Bright Zinc

A new and radically different type of zinc deposit, known as Grasselli Bright Zinc, is announced by *The Grasselli Chemical Company*. In contrast to the old electro-galvanizing, in which in most cases the deposits of zinc were dull, gray, and porous, this new process deposits zinc in a very brilliant, dense, and ductile form.

These improvements in the electro-deposition of zinc are largely the result of the use of molybdenum, a recent development of the same company. In contrast to the old methods of electro-galvanizing, this new process operates at normal room temperatures, higher current efficiencies, high or low current densities, with a bright plating range from 15–100 amperes per square foot, and provides economies unheard of in the old methods.

Basic Science Text Series

The Williams & Wilkins Company of Baltimore, Maryland, Publishers of Scientific Books and Periodicals, have concluded an arrangement with F. S. Crofts & Company, well-known college textbook publishers of New York City, for coöperative publication of basic science texts for college use. A program for new texts in the basic sciences is now being developed.

"The Wonder World of Chemistry"

The *du Pont Company* has announced that it has released for public showing an educational sound motion picture entitled "The Wonder World of Chemistry." Although the present showings will be confined to Wilmington and to the Company's exhibit at the Texas Centennial Central Exposition in Dallas, it is understood that the picture will soon be available for general distribution.

The picture is said to be the only production of its kind, and among the hundred and more shots are many types of chemical operations never before recorded for public view. Research chemists and operators are shown engaged in their daily work in the du Pont laboratories and factories. Included in the picture are such operations as the fixation of nitrogen from the air; the synthesis of a rubber-like substance from coal, limestone, and salt; the derivation of dyes and perfume materials from coal tar; the transformation of natural cellulose from cotton and wood into rayon and transparent cellulose film; the making of plastics, coated fabrics, and finishes from cotton and vegetable oils.

Du Pont officials are reported to have authorized the picture because of an increasing demand on the part of educational institutions, scientific societies, and business men's clubs for information about the company and about the chemical industry in general.

"Golden" Highways Lead Into and Out of Electrical City at Night

Golden paths of light now lead into and out of Schenectady, N. Y., at night as two of its main thoroughfares are illuminated with the golden glow of sodium lamps.

Thirty-one units on the Albany-Schenectady highway, at the city's eastern approach, and 67 similar lamps on the Western Gateway bridge, on the other side of town, were turned on during the city's recent celebration of 50 years of electrical progress.

The new units on the 5-lane Albany-Schenectady highway, between the city and county boundary lines, were turned on for the first time the same evening. They replaced 15 incandescent lamps, and the amount of light on the highway was increased from 60,000 to 300,000 lumens. Rated at 10,000 lumens each, the lamps are staggered 150 feet apart along nearly a mile of heavily traveled road.

Nearby, on the Balltown road, the first sodium lamps installed on an American highway were placed in service in 1933, after years of research by General Electric physicists and engineers, as well as thorough studies of similar developments abroad.

The 67 new light sources on the Western Gateway bridge are enclosed in ornamental luminaires. Luminous arc light sources, previously in the bridge units, have been replaced by tubular sodium lamps. With the sodium system of lighting it will be possible to operate at relatively little added cost all the lights on the bridge, according to G. E. lighting engineers, instead of alternating ones, as had been the case.

Trade Literature

CHEMICALS AND APPARATUS FOR CHEMICAL MICROSCOPY, MICROCHEMISTRY, AND MICROSCOPY. Catalog No. 100 of *R. P. Cargille, 118 Liberty St., New York City.* 4 pp., 21.5 × 28 cm.

TRENT ELECTRIC FURNACES—HIGH TEMPERATURE WITH ATMOSPHERE CONTROL. Bulletin TB-26 of *Harold E. Trent Co., 618–40 North 54th St., Philadelphia.* 2 pp., 20 × 28 cm.

PRECISION KJELDAHL EQUIPMENT FOR DIGESTIONS AND DISTILLATIONS. Bulletin 151 of *Precision Scientific Co., 1736–54 N. Springfield Ave., Chicago.* 20 pp., 21.5 × 28 cm., illustrated.

THE NEW AND REVOLUTIONARY THINGS BEING DONE IN RAYON. *Du Pont Publicity Department, Wilmington, Delaware.* 16 pp., 22 × 28.5 cm., mimeographed, paper-bound.

This bulletin contains information on the new status of rayon, and the part rayon yarns have had in creating fabric types of new excellence.

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INDUSTRY AT WORK. *Exact Weight Scale Co., Columbus, Ohio.* 32 pp., 28 × 21.5 cm. A photographic record of the multitudinous uses of Exact Weight Scales in industry.

PHOTOMICROGRAPHIC EQUIPMENT. Catalog E-21 of *Bausch & Lomb Optical Co., Rochester, N. Y.* 28 pp., 21.5 × 28 cm., illustrated. Includes discussion of "Factors in Photomicrography."

Other recent *Bausch & Lomb* publications are:

ONE LENS INVESTMENT THAT FILLS MANY NEEDS. F-130, 5, VI-36. 6 pp., 15.5 × 23.5 cm., illustrated, describing the convertible Protar lens sets.

VERSATILITY. THE BAUSCH & LOMB TESSAR. F-132, 5, V-36. 6 pp., 15.5 × 23.5 cm., illustrated.

PRICE LIST OF BAUSCH & LOMB PHOTOGRAPHIC LENSES AND ACCESSORIES. June 1, 1936. 8 pp., 15.5 × 23.5 cm.